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# PREPARATION AND INVESTIGATION OF THE PROPERTIES OF THE GALLIUM CHLORIDE - METHYLENE BLUE COMPLEX

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Complexes of gallium chlorides with organic derivatives have been studied to a comparatively small extent, which may be partly due to their instability in aqueous solutions. Thus, for example, by pouring solutions of gallium chloride in anhydrous ethylenediamine into absolute methyl alcohol, compounds of gallium chloride with 1, 2 or 3 molecules of ethylenediamine are obtained [1]. In water these compounds are unstable and on heating decompose with formation of gallium chloride. The ethylenediamine compounds of gallium are chelates and can exist as isomeric forms.

Products are obtained by interaction of gallium chloride with pyridine [2], which contain 1 or 2 molecules of pyridine per molecule of gallium chloride. These compounds dissolve in water without appreciable hydrolysis, but the molecular conductivity rapidly increases with dilution. It is assumed [3] that compounds of gallium chloride with pyridine possess the following structure  $[(C_5H_5N)_2GaCl_2] + [GaCl_4]^-$ . With the aim of stabilizing monovalent gallium, coordination compounds of  $Ga[GaCl_4]$  and  $Ga[GaBr_4]$  have been obtained [4] (empirical composition  $Ga_2X_2L_2$  where  $X = Cl, Br$  and  $L$  is a monodentate ligand), with anisole, dioxan, acetylacetone, benzoylacetone, diethylamine, aniline, etc. The resulting compounds were dimers and possessed the structure  $GaL_4^+ \cdot GaX_4^-$ . Authors explain the low stability of these gallium complexes as due to the affinity of the aromatic rings for electrons.

The best known compound of gallium chloride with an organic dye is the compound with rhodamine B [5], which is employed in the colorimetric determination of gallium. Although used for other elements precipitation by basic organic dyestuffs has not been thoroughly studied in the case of gallium.

In the present work a method for precipitating gallium chloride with the dye methylene blue is described and the results of investigation of some of the physical and chemical properties of the resultant complex are given.

## EXPERIMENTAL

Precipitation of gallium with methylene blue dye took place under conditions when the gallium was present in solution as the complex anion  $GaCl_4^-$ . Excess of chloride ion was necessary throughout the precipitation process, and therefore the dye solution used in the reaction must also contain an adequate amount of chloride ion. The precipitate formed immediately on addition of the precipitant, but for a more complete separation of the gallium, stirring the reaction mixture for 1-1.5 hr is recommended. Increasing the temperature had very little effect on the precipitation process but precipitation from solutions heated to 70-80° led to an improvement in the crystal structure of the precipitate.

The resultant precipitate was filtered onto a Buchner funnel and washed several times with 6 N hydrochloric acid in order to remove possible excess dyestuff. After this the precipitated gallium-methylene blue complex was dried to constant weight by heating at 90-95° or under vacuum without heating. Simultaneously with removal of moisture, removal of excess hydrochloric acid occluded by the precipitate takes place. The compound, dried to constant weight, was subjected to chemical analysis to determine its composition. The gallium, chlorine and dye contents were determined. The analytical results are reported in Table 1, where for comparison calculated figures for the assumed composition of the complex are given in the first column.

From Table 1, it is seen that the analytical results are in good agreement with the calculated figures. This leads to the conclusion that the empirical composition of the compound is the following:  $[C_{16}H_{18}N_3SGaCl_4]$ .



Determination of the molecular weight of the gallium chloride-methylene blue complex was carried out cryoscopically in water. The resulting value for the depression of freezing point was found to be 6 times greater than the figure calculated on the assumption that there are no reactions in aqueous solution. Thus the expected depression was 0,048, but the experimentally found figure was 0,288. If it is assumed that the compound dissociates into six ions ( $C_{16}H_{18}N_3S^+ + Ga^{+3} + 4Cl^-$ ), then the molecular weight determined cryoscopically is in agreement with the calculated value. The calculated mole weight is 493,73; the experimentally found value is 495,98.

TABLE 1

Component of Compound	Assumed Composition %	Analytical Results %
Gallium	14,06	14,10
Chlorine	28,60	28,60
Dye including:	57,32	57,40
Carbon	38,75	38,82
Hydrogen	3,63	3,41
Nitrogen	8,47	8,55

TABLE 2

Dilution	Concentration 1/M	Conductivity	
		Specific	Molecular
1 : 1	100	0,0041	410
1 : 2	200	0,00227	454
1 : 4	400	0,00135	541
1 : 8	800	0,000786	624

Measurement of the specific conductivity of aqueous solutions of the complex at different dilutions was carried out in a thermostat at 25°. The molecular conductivity was calculated at the same time. The results showing the change in conductivity with dilution are given in Table 2.

From Table 2 it is seen that there is a straight line relationship between the specific conductivity and the dilution, indicating complete dissociation of the compound in aqueous solution.

The change in the molecular conductivity shows that on eight-fold dilution it attains the value of 624 corresponding to the presence of six ions in solution (according to Werner's empirical rule) [6]. Consequently the postulated formation of six ions in aqueous solution appears correct and the experimentally obtained value for the molecular weight of the compound confirms the correctness of the empirical formula of the complexes.

Investigation of the behavior of the compound in various solvents was carried out in a thermostat at 25°. Samples of the liquid and solid phases were withdrawn after five and ten days from the date of charging the vessel. The agreement of the analytical results showed that equilibrium is already reached after five days. The phases were analyzed for gallium, chlorine and dyestuff. The analytical data are given in Table 3.

The data of Table 3 indicate that insignificant solution of the compound occurs in ethyl alcohol, 6 N hydrochloric acid solution, and 5 N sulfuric acid saturated with sodium chloride. In the rest of the solvents the complex is destroyed since the percentage proportions of the elements of the compound in the solid and liquid phases do not correspond to the stoichiometric composition of the compound in the solid state (gallium 14,06; chlorine 28,6; dye 57,32).

The minimum solubility of the compound occurs in 6 N hydrochloric acid and in 5 N sulfuric acid saturated with sodium chloride. According to the decrease in acidity the compound is decomposed with predominant transfer of gallium into the liquid phase, while the amount of the dye passing into solution remains at around 5-6%. Maximum extraction of gallium into the liquid phase is observed for water. The amount of gallium passing into the aqueous solution is 91,5% and for the dyestuff is 1,15%. It may be assumed that in a saturated aqueous solution of the gallium-methylene blue compound hydrolytic decomposition of the compound occurs with partial replacement of the  $GaCl_4^-$  anion in the dyestuff molecule with  $Cl^-$  or  $OH^-$  ions.

At the same time the solubility of pure dye in certain solvents was studied. The results are given in Table 4.

In order to be satisfied that in solution (liquid phases) formation of new complexes does not occur, measurement was made of the light absorption of solutions of the pure dye and its compound with gallium on the SF-4 spectrophotometer. The light absorption curves possess maxima at the same wavelength corresponding to the maximum for the light absorption of the pure dye. Consequently the complex compound  $[C_{16}H_{18}N_3SGaCl_4]$  on solution in water, methyl alcohol, and acetone is dissociated and no additional complex formation occurs.

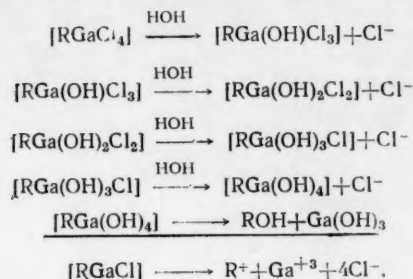
Study of the behavior of the complex compound in saturated solutions showed the instability of this compound in the presence of  $OH^-$  ions. On determination of the pH of aqueous solutions of the compound at 20° in relation to the dilution, an increase of the pH value and appreciable increase of the degree of hydrolysis (Table 5) are detected.

TABLE 3

Solvent	Liquid Phase			Solid Phase		
	Composition, %			Composition, %		
	Ga	Dye	Cl	Ga	Dye	Cl
Water	2.78	1.03	4.43	91.50	1.15	13.50
Bnvl alcohol	0.066	0.40	0.27	0.46	0.69	0.94
6 N HCl	0.02	0.82	0.26	0.17	1.45	0.89
3 N HCl	0.10	3.50	1.43	0.55	6.15	4.80
3 N H <sub>2</sub> SO <sub>4</sub>	1.85	4.70	3.81	31.60	5.20	26.60
5 N H <sub>2</sub> SO <sub>4</sub>	4.23	2.30	2.56	19.60	2.64	20.40
Acetone	0.29	1.90	0.95	2.96	2.57	5.10
Benzene	—	—	—	—	—	—
5 N H <sub>2</sub> SO <sub>4</sub> , saturated NaCl (3.35 N Cl)	0.040	0.4	0.010	0.28	0.69	0.035
				14.30	57.3	28.4
				0.34	88.6	10.9
				14.30	57.4	28.3
				15.30	55.7	29.0
				18.20	53.4	28.5
				4.01	88.5	10.5
				5.20	84.8	10.0
				9.50	72.8	17.7
				14.00	58.3	27.7
				14.30	57.3	28.4
				8.50	98.85	86.50
				99.54	99.31	99.05
				99.83	98.55	99.11
				99.45	93.85	95.20
				68.40	94.80	73.60
				80.90	97.36	79.60
				94.90	97.43	94.90
				100.0	100.0	100.0
				99.72	99.31	99.96

Increase of the degree of hydrolysis with dilution shows that the compound is hydrolyzed rather extensively and at very low concentrations of the complex and large concentrations of OH<sup>-</sup> ions the degree of hydrolysis is close to unity i.e., the compound is completely hydrolyzed.

Comparison of the hydrolysis results with the values of the molecular conductivity in relation to the dilution (cf. Table 2) suggests the following mechanism of stepwise hydrolysis



where R is the dyestuff cation  $[\text{C}_{16}\text{H}_{18}\text{N}_3\text{S}]^+$ .

The concentration of gallium in very dilute solutions does not reach the value of the solubility product of gallium hydroxide and separation of a precipitate does not occur.

Potentiometric titrations of an aqueous solution of the complex and of the original gallium chloride and dyestuff solutions were carried out with use of a glass electrode, and the pH values during titration were measured on a LP-5 potentiometer. The titration was carried out with 0.1 N NaOH solution. The titration curves are given in Fig. 1.

The titration curve 1 for the dye solution showed that the rapid rise in the curve corresponded to addition of one equivalent of NaOH, after which a constant pH value is maintained, not depending on the amount of alkali added. This is explained by the fact that after neutralization of the chloride ion associated with the dye a compound is formed which is stable over a wide range of pH. With a 15-20% alkalinity of the solution substitution of one of the  $\text{N}(\text{CH}_3)_2$  groups by an OH<sup>-</sup> group occurs and the dye separates in the precipitate with complete decolorization of the solution. During titration of gallium chloride solution (curve 3) separation of gallium hydroxide is initially observed at pH 3 and complete solution of the hydroxide occurs at pH 11.7.

The results of the titration of a solution of the complex (curve 2) are significantly different from the results obtained for the two primary solutions. Addition of alkali up to two equivalents does not cause a sharp change in the titration curve and only on adding a third equivalent (pH 3.69) does a sharp change begin to show, caused by the onset of formation of gallium hydroxide. The sharp rise of the curve is continued until pH 12 is reached, corresponding to completion of the solution of gallium hydroxide and the rest of the curve runs parallel to the ordinate axis.

Change in the pH with initial formation of hydroxide, from 3 to 3.69, indicates the presence of gallium bonded with the dye

molecule for the decomposition of which an additional quantity of alkali is required compared with a solution of pure gallium chloride. Consumption of two equivalents of alkali is required to displace two chlorine atoms from the saturated coordination sphere, and addition of a third equivalent of NaOH leads to formation of  $\text{Ga}(\text{OH})_3$  which at the appropriate gallium concentration separates out as a precipitate [cf. equations (1), (2), and (3)].

TABLE 4

Solvent	Solubility g in 100 g of solution
Water	13,70
Methyl alcohol	5,20
Ethyl alcohol	2,30
Dimethylformamide	1,30
Acetone	0,024
Benzene	Not soluble
Tetrachloromethane	" "

TABLE 5

Dilution l/M	pH	Degree of hydrolysis
100	2,55	0,280
200	2,790	0,325
400	2,860	0,552
800	2,980	0,840

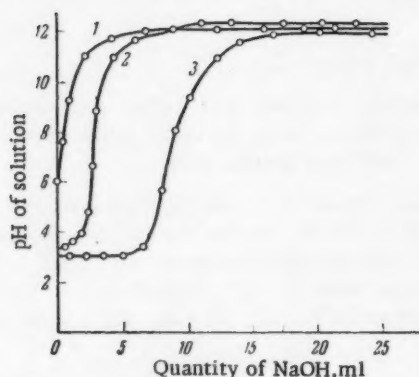


Fig. 1. Potentiometric titration curves of 1) methylene blue dye solution; 2) gallium chloride-methylene blue complex solution; 3) gallium chloride solution.

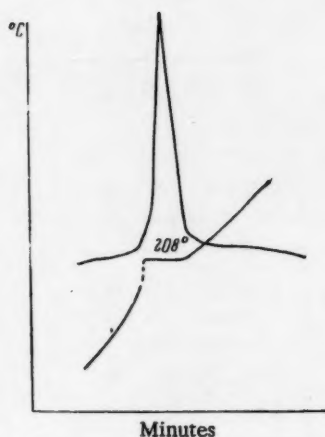


Fig. 2. Thermogram of the gallium chloride-methylene blue complex.

TABLE 6

Element	Original Composition %	Composition in % after drying at °C			
		100	200	230	300
Carbon	38,82	38,82	38,82	39,45	41,45
Nitrogen	8,55	8,55	8,55	6,05	4,83
Hydrogen	3,41	3,41	3,41	2,84	1,61
Chlorine	28,60	28,60	28,60	29,98	23,00

The melting point of the gallium chloride-methylene blue complex is  $208 \pm 2^\circ$  determined on the "block." A thermogram of the substance taken on the Kurnakov pyrometer, showed that after reaching  $208^\circ$  a large exothermic effect is observed which indicates that soon after melting the compound burns with a large liberation of heat.

For a more accurate determination of the temperature limits of the existence of the complex, experiments were carried out on the compound dried to constant weight at various temperatures. On attainment of constant weight the substance was subjected to analysis with the object of establishing the loss during drying. The analytical results are given in Table 6.



Experiments to determine the thermal stability of the compound indicate that on heating to 200° the composition of the complex is not changed. On heating above 200° gradual decomposition of the complex occurs. Thus, at 230° nitrogen and hydrogen are eliminated from the organic part of the complex, whereby the carbon and chlorine content increases. At 300° together with nitrogen and hydrogen, chlorine begins to be eliminated. At a temperature of 500° decomposition of the complex has ended since further increase of the temperature to 800, 900 and 1000° is not reflected in the weight of the heated substance. Analysis of the substance calcined at 500° and above showed that it consists of 100% gallium oxide, the gallium having been quantitatively converted to the oxide.

It may be assumed that up to 500° reduction of the gallium to the metal occurs owing to the carbon, formed during decomposition of the organic part of the molecule. The metal oxidizes to form the oxide. Elimination of chlorine occurs, without effecting the gallium and sublimation of gallium as the chloride during calcination does not occur.

#### SUMMARY

1. A new compound of gallium chloride with the dye methylene blue of composition  $[C_{16}H_{18}N_3SGaCl]_4$  was synthesized.
2. The behavior of the compound in different media was studied.
3. The thermal stability of the compound was determined.

#### LITERATURE CITED

1. A. P. Kochetkova and V. G. Tronev, *Zh. neorgan. khimii* 2, 2043 (1957).
2. B. N. Ivanov-Émin and E. A. Ostroumov, *Zavodsk. Laboratoriya* 12, 674 (1946).
3. N. N. Greenwood and K. Wade, *J. Chem. Soc.*, 1958, 1663.
4. S. M. Ali, F. M. Brewer, J. Chodwick, and G. Garton, *J. Inorg. and Nucl. Chem.* 9, No. 2, 124 (1959).
5. H. Onishi, *Analyt. Chem.* 27, 832 (1955).
6. A. Werner, *New Horizons in the Field of Inorganic Chemistry* [Russian translation] (ONTI, Leningrad, 1936).

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. Some or all of this periodical literature may well be available in English translation. A complete list of the cover-to-cover English translations appears at the back of this issue.

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## THE FORMATION OF MAGNESIUM HYDROXIDE

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The formation of hydroxides of the group II elements (the beryllium subgroup), particularly magnesium, has not been, so far, examined thoroughly enough. It was therefore of a considerable theoretical and practical interest to elucidate the mechanism of the formation of magnesium hydroxide and compare it with the formation of other hydroxides, particularly the hydroxides of other beryllium subgroup elements. Using physicochemical analytical methods we investigated systems of the type  $MgA_2 + NaOH + H_2O$ , where  $A = Cl^-, NO_3^-, \frac{1}{2}SO_4^{2-}$ .

### EXPERIMENTAL

The initial concentration of the magnesium salt (chloride, nitrate, or sulfate) was either 0.02 or 0.10 M in all of our mixtures, thus covering the concentration range most frequently encountered in chemical problems. The  $MgSO_4 + NaOH + H_2O$  system was also studied by using solutions in which the  $MgSO_4$  concentrations were 0.6, 0.8, and 0.9 M. The initial NaOH concentration was increased in successive experiments. The equilibrium was attained by stirring the mixtures for 5 hr (with an electric stirrer) in 50 ml graduated cylinders (with a water seal) placed in a thermostat at a temperature of  $25 \pm 0.1^\circ C$ .

After 24 hr we determined the volume of solid precipitated by reading the column height off the cylinder. Subsequently the liquid phase was separated from the solid by filtering the mixture through a double filter ("blue ribbon" brand).

Analysis of the liquid phase. At first one aliquot was analyzed qualitatively for  $Mg^{++}$  by means of quinalizarin (theoretically free ions are expected until  $n = NaOH:MgA_2 = 2$ )\* and for  $OH^-$  by using phenolphthalein (when  $n > 2$ ). Using 25 ml aliquots we determined the  $Mg^{++}$  concentration by means of trilon-B[1] and the  $OH^-$  by titration with 0.1 N hydrochloric acid to a methyl orange end-point.

Analysis of the solid phase. The filter paper with the solid was placed on a suction funnel and washed with acetone to remove traces of  $MgCl_2$  or  $Mg(NO_3)_2$  and NaOH, or with an acetone-water (1:1) mixture to remove  $MgSO_4$ . After that a weighed portion of the solid was dissolved\*\* in an excess of 0.1 N hydrochloric acid in a beaker; the solution was then transferred to a 100 ml volumetric flask and made up to volume with water. One aliquot of the resulting solution (40 ml) was back-titrated with sodium hydroxide to determine the excess acid; another equivalent aliquot was neutralized with a base of known concentration (without using any indicator) and the  $Mg^{++}$  concentration was determined by titration with a trilon-B solution. It should be noted that precipitates obtained when  $Mg^{++}$  is in excess ( $n \leq 2$ ) dissolve readily in boiling acid. But precipitates obtained when  $OH^-$  is in excess ( $n > 2$ ) seem more dense and cannot be dissolved as readily in acids.

After analyzing the liquid phase we calculated the composition of the precipitate (the  $OH^-:Mg^{++}$  ratio) from the difference between the initial amounts of components and the amounts found in the liquid. On the other hand analysis of the solid gave us directly the amount of  $OH^-$  and  $Mg^{++}$ . In neither case was the amount of water of hydration retained in the solid determined. The pH of the liquid phase aliquots was determined potentiometrically on an LP-5 instrument using calomel and glass electrodes.

We used both the indirect determination of precipitate volume proposed by Tananaev [2] and our own method [3], in which after 5 hr of equilibration the mixture is left standing and the precipitate volume measured after 24 hr.

\* From now on we will use the letter  $n$  to denote the initial  $NaOH:MgA_2$  ratio.

\*\* If the amount of precipitate was small the entire solid was dissolved directly on the filter paper right after washing.

In Tananaev's work the mixtures were placed in 25 ml test tubes and shaken by hand for 20 min; the precipitate volume was measured after the system was left standing for time intervals of 1, 24, and 48 hr. Both the mixing and the volume determination were done at room temperature (20°). Finally, as in all of our other measurements, we constructed a diagram with the precipitate volume given on the ordinate and  $n$  on the abscissa.

## EXPERIMENTAL

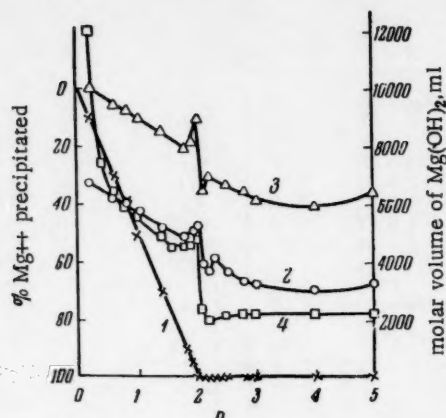


Fig. 1. Reaction between the components of the system  $\text{MgA}_2 + \text{NaOH} + \text{H}_2\text{O}$  (from liquid phase analysis): 1) initial  $\text{MgA}_2$  concentration 0.02-0.1 M. Change in the molar volume of the  $\text{Mg}(\text{OH})_2$  precipitate in the systems: 2)  $\text{MgCl}_2 + \text{NaOH} + \text{H}_2\text{O}$ ; 3)  $\text{Mg}(\text{NO}_3)_2 + \text{NaOH} + \text{H}_2\text{O}$ ; 4)  $\text{MgSO}_4 + \text{NaOH} + \text{H}_2\text{O}$ . The initial concentrations of the magnesium salts were 0.10, 0.02, and 0.10 M respectively.

The results obtained from the liquid-phase analysis of the systems:  $\text{MgCl}_2 + \text{NaOH} + \text{H}_2\text{O}$ ,  $\text{Mg}(\text{NO}_3)_2 + \text{NaOH} + \text{H}_2\text{O}$ , and  $\text{MgSO}_4 + \text{NaOH} + \text{H}_2\text{O}$  are presented in Tables 1-3 and Fig. 1. The precipitation curve in Fig. 1 shows that precipitation occurs at all values of  $n$  from 0.2 to 5.0, since the solubility of  $\text{Mg}(\text{OH})_2$  in water is  $1 \cdot 10^{-4}$  M. One can also see that we get a straight line instead of a curve in this case. This last observation indicates that: 1) the precipitation follows the predicted course; 2) the process is independent of excess  $\text{Mg}^{++}$  or  $\text{OH}^-$  ions in solution, and 3)  $\text{Mg}(\text{OH})_2$ ,  $\text{MgA}_2$ , and  $\text{NaOH}$  do not form solid solutions or any basic or complex salts.

Since introduction of neutral  $\text{NaF}$  does not increase the alkalinity of the liquid phase,\* one may conclude that no soluble basic salts are formed either. The data presented in Tables 1-3 show that there is no significant coprecipitation of  $\text{NaOH}$  with  $\text{Mg}(\text{OH})_2$  until  $n = 2$  is attained.

Our data clearly indicate that magnesium can be determined analytically by adding sodium hydroxide to precipitate magnesium hydroxide and back-titrating the excess base in the filtrate; a hydroxide concentration can likewise be determined by titrating an excess of one of our magnesium salts. In order to avoid errors caused by the solubility of  $\text{Mg}(\text{OH})_2$  in water when one determines magnesium gravimetrically (by forming  $\text{Mg}(\text{OH})_2$  and converting it by heating to  $\text{MgO}$ ) it is customary to wash the

filtrate with acetone instead of water. In a volumetric determination of magnesium after  $\text{Mg}(\text{OH})_2$  is precipitated in a volumetric flask aliquots of the filtrate (coprecipitate) are used for analysis. While one can safely forget about the application of the discussed method to the determination of alkalinity the analytical aspects of the simple magnesium determination discussed above deserve more attention since the currently used gravimetric (pyrophosphate) and volumetric (a variation of the hydroxyquinoline method) methods are quite involved. Successful, though unfortunately neglected, magnesium determinations based on the precipitation by excess alkali have been reported by other workers [4, 5] and tend to support our data. We would like to point out that in addition to  $\text{Mg}(\text{OH})_2$  (precipitated from solutions of chloride, sulfate, and nitrate) other hydroxides can also be precipitated without carrying along any excess hydroxide ion; silver [6] and zinc [7] from solutions of their nitrates and cadmium [8] from a solution of its sulfate have been thus precipitated.

The solid-phase analytical data presented in Table 4 are in complete agreement with the corresponding liquid-phase data. The solid-phase data from the investigated systems show that washing with acetone will remove any excess of magnesium salt or sodium hydroxide entirely.

The data obtained from the pH determination are presented in Tables 1-3 and plotted in Figs. 2-4. The figures show that the pH curves for our systems resemble potentiometric titration curves and the inflection point at  $n = 2$  corresponds to the complete precipitation of magnesium in the form of  $\text{Mg}(\text{OH})_2$ . The pH curves also confirm the fact that no other intermediate complexes are formed in our systems. We should note that  $\text{Mg}(\text{OH})_2$  is completely precipitated at  $\text{pH} = 10.9-11.0$  [9] and the solubility of  $\text{Mg}(\text{OH})_2 = 1 \cdot 10^{-4}$  M. Consequently it is obvious that magnesium can be titrated potentiometrically with sodium hydroxide.

\* If a reaction such as  $\text{Mg}(\text{OH})\text{Cl} + 2\text{NaF} \rightleftharpoons \text{MgF}_2 + \text{NaOH} + \text{NaCl}$  took place the phenolphthalein would turn red.

TABLE 1. Liquid-Phase Analytical Data for the System  $\text{MgCl}_2 + \text{NaOH} + \text{H}_2\text{O}$ , the Effective Volume of the Precipitate, and the pH. (The initial  $[\text{MgCl}_2] = 0.1 \text{ M}$ , or 5.0 mmoles/50 ml of investigated solution)

n	Liquid phase analysis			Ppt. volume (ml) with time (hr)				
	Pptd., moles · 10 <sup>4</sup>		OH <sup>-</sup> :Mg <sup>++</sup> in the ppt	24	1	24	48	pH
	OH	Mg <sup>++</sup>						
0,2	10,00	4,90	2,04	3,4	Suspension	1,30	1,70	7,67
0,6	30,00	14,75	2,03	9,4	»	3,70	4,15	7,93
0,8	40,00	19,73	2,03	12,0	»	4,25	5,80	8,00
1,0	50,00	25,27	1,98	14,4	»	5,30	6,70	8,10
1,4	70,01	35,00	2,00	18,4	23,4	4,47	8,60	8,15
1,8	90,20	44,00	2,05	22,0	24,9	6,93	10,50	8,17
1,9	95,00	47,00	2,02	24,0	24,6	6,47	8,70	8,55
2,0	100,00	50,00	2,00	26,3	24,8	7,54	7,80	10,87
2,1	102,00	50,00	2,04	19,3	24,75	5,54	7,20	11,20
2,2	100,00	50,00	2,00	18,8	24,75	6,16	8,90	11,40
2,3	102,55	50,00	2,05	20,8	Suspension	5,80	8,50	11,75
2,5	101,66	50,00	2,03	18,2	24,80	6,20	8,00	11,90
2,8	101,28	50,00	2,03	16,6	24,60	5,63	7,40	12,03
3,0	102,50	50,00	2,05	16,2	24,70	5,53	7,20	12,10
4,0	100,53	50,00	2,01	15,0	Suspension	6,25	6,50	12,12
5,0	102,26	50,00	2,04	16,3	24,10	5,20	6,60	12,12

TABLE 2. Liquid-Phase Analytical Data for the System  $\text{Mg}(\text{NO}_3)_2 + \text{NaOH} + \text{H}_2\text{O}$ , the Effective Volume of the Precipitate, and the pH. (The initial  $[\text{Mg}(\text{NO}_3)_2] = 0.02 \text{ M}$ , or 1.0 mmole/50 ml of investigated solution)

n	Liquid phase analysis			Ppt. volume (ml) with time (hr)				pH
	Pptd., moles·10 <sup>4</sup>		OH:Mg <sup>++</sup> in the ppt	24	1	24	48	
	OH <sup>-</sup>	Mg <sup>++</sup>						
0,2	2,00	1,00	2,00	1,0	Colloid	0,45	0,50	8,35
0,6	6,00	3,00	2,00	2,9	1,40	1,50	1,60	8,60
0,8	8,00	3,94	2,03	3,7	Colloid	2,00	2,10	8,70
1,0	10,01	5,12	1,96	4,5	"	2,40	2,70	8,77
1,4	14,02	6,94	2,02	6,0	19,00	3,20	3,75	8,90
1,8	17,93	8,69	2,06	7,2	19,70	3,70	4,40	9,07
1,9	19,09	9,36	2,04	7,8	19,70	3,85	4,80	9,14
2,0	20,00	10,00	2,00	9,0	19,60	3,90	4,30	9,46
2,1	19,82	10,00	1,98	6,5	21,10	3,45	4,70	10,85
2,2	20,00	10,00	2,00	7,0	20,20	3,35	4,80	11,31
2,5	20,49	10,00	2,05	6,7	22,60	3,40	4,60	11,67
2,8	19,94	10,00	1,99	6,5	21,00	3,00	4,15	11,87
3,0	20,36	10,00	2,04	6,2	21,20	3,10	4,20	11,93
4,0	20,45	10,00	2,05	6,0	21,10	3,00	4,10	12,08
5,0	21,21	10,00	2,12	6,5	16,40	2,20	4,00	12,12

The experimental results from the effective precipitate volume determinations for the systems:  $\text{MgCl}_2 + \text{NaOH} + \text{H}_2\text{O}$ ,  $\text{Mg}(\text{NO}_3)_2 + \text{NaOH} + \text{H}_2\text{O}$ , and  $\text{MgSO}_4 + \text{NaOH} + \text{H}_2\text{O}$  are also presented in Tables 1-3, and plotted in Figs. 2-4. The leftmost column under the heading "precipitate volume" (Tables 1-3) gives the volumes of the precipitates determined by our method [3] after a time interval of 24 hr in experiments where both the liquid and the solid phase of equilibrated systems were analyzed; immediately to the right of this column, precipitate volume determined after 1, 24, and 48 hr of standing (the Tananaev method [2]) are given. Tables 1-3 show the settling (aging) kinetics of the  $\text{Mg}(\text{OH})_2$  precipitates in our system. One can see that there is very little difference between the precipitate volumes determined after 24 and 48 hr, indicating that the settling of  $\text{Mg}(\text{OH})_2$  is practically complete within 24 hr. This is also confirmed by the fact that in analyzing solids aged for more than 24 hr it is very difficult to dissolve them even in hot acids.

The maximum observed on the precipitate volume curves at  $n = 2$  corresponds to the composition of magnesium hydroxide. The slight discrepancy between the curves based on data obtained in experiments using Tananaev's method



and those we get by our method can be attributed to the fact that in our case precipitate volumes in systems at equilibrium were determined while in the other method we are dealing with nonequibrated systems. Other factors contributing to this discrepancy are the differences between the wall areas and diameters of the measuring vessels and the different ways in which the components were added to each other.

TABLE 3. Liquid-Phase Analytical Data for the System  $\text{MgSO}_4 + \text{NaOH} + \text{H}_2\text{O}$ , the Effective Volume of the Precipitate, and the pH. (The initial  $[\text{MgSO}_4] = 0.1 \text{ M}$ , or  $5.0 \text{ mmol}/50 \text{ ml}$  of investigated solution)

n	Liquid phase analysis			Ppt. volume (ml) with time (hr)				pH
	Pptd., moles · 10 <sup>4</sup>		OH ; Mg <sup>++</sup> in the ppt	24	1	24	48	
	OH <sup>-</sup>	Mg <sup>++</sup>						
0,2	10,00	5,00	2,00	6,0	Suspension	0,95	0,80	8,45
0,4	19,99	9,79	2,04	7,4	—	—	—	8,50
0,6	30,00	15,00	2,00	9,6	17,50	2,24	1,90	8,60
0,8	40,00	19,87	2,01	11,8	19,60	2,90	2,49	8,75
1,0	50,00	24,73	2,02	14,0	23,20	3,60	3,20	8,87
1,4	70,00	35,00	2,00	17,2	24,70	4,60	4,15	9,06
1,6	80,00	40,26	1,99	18,2	—	—	—	9,25
1,8	90,00	45,21	1,99	21,0	25,00	6,90	6,00	9,35
1,9	95,00	47,61	2,00	22,0	25,00	7,10	5,75	9,40
2,0	100,00	50,00	2,00	24,0	25,00	5,20	4,90	10,60
2,1	100,31	50,00	2,01	11,5	25,00	4,70	4,70	11,65
2,2	101,50	50,00	2,03	10,1	24,90	4,90	5,30	11,95
2,5	101,64	50,00	2,03	10,6	24,85	4,90	5,30	12,10
2,8	101,60	50,00	2,03	11,0	24,95	5,23	5,35	12,11
3,0	101,21	50,00	2,02	11,0	24,95	5,33	5,40	12,12
4,0	105,42	50,00	2,11	11,0	—	—	—	12,13
5,0	105,87	50,00	2,12	11,2	—	—	—	12,14

TABLE 4. Solid-Phase Analytical Data. (Initial  $\text{Mg}(\text{NO}_3)_2$  and  $\text{MgSO}_4$  concentrations were  $0.1 \text{ M}$ )

The system $\text{Mg}(\text{NO}_3)_2 + \text{NaOH} + \text{H}_2\text{O}$				The system $\text{MgSO}_4 + \text{NaOH} + \text{H}_2\text{O}$			
n	Found, moles $\cdot 10^4$		$\text{OH}^- : \text{Mg}^{++}$ in the ppt	n	Found, moles $\cdot 10^4$		$\text{OH}^- : \text{Mg}^{++}$ in the ppt
	$\text{OH}^-$	$\text{Mg}^{++}$			$\text{OH}^-$	$\text{Mg}^{++}$	
0,2	3,95	1,90	2,08	0,4	6,76	3,33	2,04
0,6	8,69	4,31	2,02	0,8	10,33	5,24	1,97
0,8	10,47	5,07	2,06	1,0	21,76	10,61	2,05
1,0	5,26	2,76	1,91	1,6	12,00	6,00	2,00
1,4	6,98	3,68	1,90	1,8	19,22	9,53	2,02
1,8	8,83	4,30	2,05	1,9	19,60	9,89	1,98
1,9	9,34	4,52	2,07	2,0	37,00	18,47	2,00
2,0	9,19	4,67	1,97	2,1	23,01	11,56	1,99
2,1	13,69	6,91	1,98	2,5	13,02	6,55	1,99
2,2	14,70	7,61	1,93	3,0	12,78	6,32	2,02
2,5	9,44	4,60	2,05				
2,8	7,44	3,62	2,06				
3,0	9,46	4,73	2,00				
4,0	12,34	5,93	2,08				

The molar volume measurements (see Fig. 1)\* show that the looseness of the  $\text{Mg}(\text{OH})_2$  precipitate is proportional to the concentration of excess  $\text{Mg}^{++}$  in the supernatant liquid, i.e., as  $n$  increases the  $\text{Mg}(\text{OH})_2$  precipitate gradually becomes more compact until  $n = 1.8$  is reached. Only in the range  $n = 1.8-2.0$  does the density of  $\text{Mg}(\text{OH})_2$

\* We did not bother to reproduce the figures showing the changes in the molar volumes of  $\text{Mg}(\text{OH})_2$  precipitates obtained in the other systems investigated by us due to their similarity with Fig. 1. If necessary these curves can be readily reproduced by plotting the tabulated volume data. The molar volumes of  $\text{Mg}(\text{OH})_2$  precipitates were calculated from data obtained in the described manner.

slightly decline. But in the range  $n = 2.0-2.2$  the density of the  $Mg(OH)_2$  precipitate sharply increases under the influence of the  $OH^-$  ions.

The minima observed on the precipitate volume curves at  $n = 1.8$  and  $n = 2.2$  and the maxima at  $n = 2.3-2.8$  do not correspond to any definite chemical compounds (as has been shown by three different experimental methods) but can be attributed to the effects of various magnesium and hydroxide concentrations on the degree of dispersion of the  $Mg(OH)_2$  precipitate. For example, as one approaches  $n = 2.2$  the density of  $Mg(OH)_2$  precipitate sharply increases under the influence of excess  $OH^-$ , then some loosening occurs (apparently as a result of a partial peptization brought about by increased concentration of alkali), and finally the density rises again attaining a maximum in the range  $n = 2.3-2.8$ ; subsequently there is practically no change in the density of the  $Mg(OH)_2$  precipitate as  $n$  increases from 2.8 to 5.0.

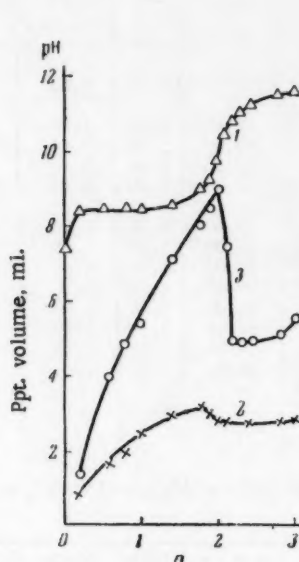


Fig. 2.

Fig. 2. Changes in the pH (1) and precipitate volume; 2) determined by the Tananaev method; 3) by our method, in the system  $MgCl_2 + NaOH + H_2O$ . The initial  $[MgCl_2] = 0.02$  M.

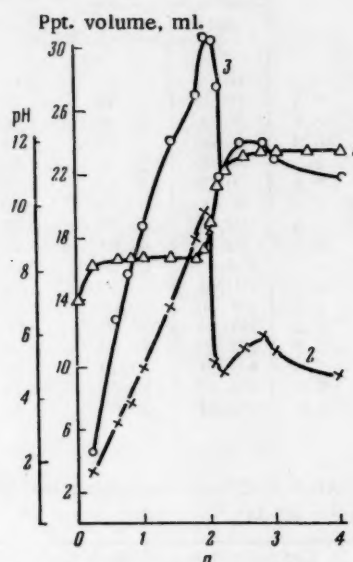


Fig. 3.

Fig. 3. Changes in the pH (1) and the precipitate volume; 2) determined by the Tananaev method; 3) by our method, in the system  $Mg(NO_3)_2 + NaOH + H_2O$ . The initial  $[Mg(NO_3)_2] = 0.1$  M.

The  $Mg(OH)_2$  has the least molar volume in the range  $n = 2.0-2.2$  and  $3.0-5.0$ . Hence from the observed changes in the precipitate volume one can determine at what  $n$   $Mg(OH)_2$  precipitate occupies least space (is most compact) which may be of some technological value and of use in analytical chemistry. As a rule most hydroxides do not precipitate as simple hydroxides. For example, when the hydroxides of the beryllium subgroup elements: beryllium [2, 10], zinc [7, 11], cadmium [7, 8], and mercury [7] are precipitated from chloride or sulfate solutions they all pass through a basic salt stage.

The experimental data obtained by various methods indicate that in the systems:  $MgCl_2 + NaOH + H_2O$ ,  $Mg(NO_3)_2 + NaOH + H_2O$ , and  $MgSO_4 + NaOH + H_2O$ , in the magnesium salt concentration range from 0.02-0.10 M, regardless of which salt is used the hydroxide is formed by the same "ideal" mechanism (one which rigorously agrees with the calculated data), and that at all values of  $n$  only one compound  $[Mg(OH)_2]$  is formed in all the investigated systems. The precipitation of the hydroxide of a metal such as magnesium according to the "ideal" mechanism when aqueous alkali react with three different salts of the same metal (chloride, nitrate, and sulfate in this instance) represents a unique case. Up till now only three hydroxides have been known to precipitate by the "ideal" mechanism,

those of: silver [6], zinc [7], and divalent nickel [12], though only from one kind of salt (nitrate) and at concentrations smaller than 0.025, 0.1, and 0.01 M respectively. But if the  $\text{Ni}(\text{NO}_3)_2$  concentration exceeds 0.01 M the precipitation of the hydroxide does not follow the "ideal" mechanism [12]. Thus the "ideal" precipitation of hydroxides has an upper (or maximum) salt concentration limit above which the precipitation proceeds nonideally.

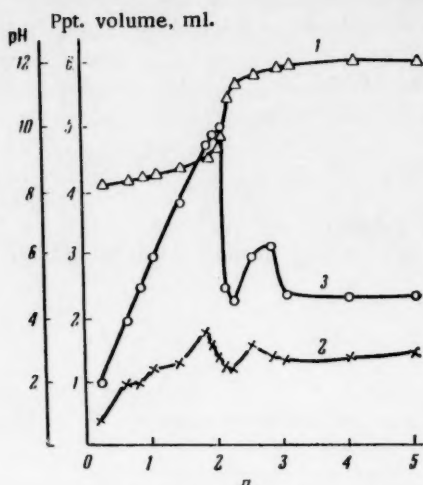


Fig. 4. Changes in the pH (1) and precipitate volume; 2) determined by Tananaev's method; 3) by our method in the system  $\text{MgSO}_4 + \text{NaOH} + \text{H}_2\text{O}$ . The initial  $[\text{MgSO}_4] = 0.02 \text{ M}$ .

Magnesium hydroxide resembles the hydroxides of silver and divalent nickel in that it is distinctly basic, and hence no basic salts are formed, so that magnesium precipitates directly in the form of  $\text{Mg}(\text{OH})_2$  without adsorbing any excess of base. As an exception we can cite zinc hydroxide which through amphoteric does not form a basic salt or carry along an excess base when precipitated from a nitrate solution. Other distinctly basic hydroxides such as those of: cadmium, mercury, trivalent cerium [13], neodymium [14], thorium [15] do form basic salts but do not carry along any appreciable quantity of excess hydroxide.

Weakly amphoteric hydroxides, such as zirconium [16] and titanium [3] hydroxides, in addition to forming basic salts absorb large amounts of alkali greatly in excess of the amounts absorbed by distinctly basic salts. Whenever a hydroxide is distinctly amphoteric before one reached the stage at which the precipitate redissolves completely in excess alkali considerable absorption of hydroxide ion by the precipitated hydroxide is observed as in the case of beryllium, zinc (from chloride and sulfate), and aluminum hydroxides [17]. After examining the reactions studied by us we can conclude that the mechanism of hydroxide precipitation in most cases depends on the nature and initial concentrations of the cations and anions.

It should be noted that up till now the mechanism and kinetics of metal hydroxide precipitation (aging) were investigated simultaneously by just one method, namely by measuring the apparent precipitate volume. It is obvious that a full understanding of the hydroxide precipitation reactions will eventually be achieved, but only after the reaction mechanism and kinetics have been examined by other physicochemical methods.

#### SUMMARY

1. The system  $\text{MgA}_2 + \text{NaOH} + \text{H}_2\text{O}$  (25°), where  $\text{A} = \text{Cl}^-$ ,  $\text{NO}_3^-$ , or  $\frac{1}{2}\text{SO}_4^{2-}$ , have been examined by means of liquid and solid phase analysis, by the determination of the apparent precipitate volume, and by following pH changes. The only product formed in these systems was magnesium hydroxide; no basic or other type complexes were found.

2. Magnesium hydroxide precipitated in solutions where the initial ratio of  $\text{NaOH}:\text{MgA}_2 = 4$ , is not exceeded, does not carry along any excess hydroxide ion, and therefore magnesium can be determined quantitatively (gravimetrically, volumetrically, and potentiometrically) by a precipitation in excess alkali.

3. From the measurements of precipitate volume in the investigated systems one can decide on the optimum conditions for producing the most compact magnesium hydroxide which may be of some technological value and of use in analytical chemistry.

#### LITERATURE CITED

1. Coll. Complexometry, Theoretical Basis and Practical Applications [In Russian] GONTI, Moscow, 1958, p. 84.
2. I. V. Tananaev, *Izv. Sektora Fiz.-Khim. Analiza* **20**, 288 (1950).
3. A. I. Ul'yanov, *Izv. AN SSSR, Otd. Khim. Nauk* **1960**, 580.
4. N. A. Tananaev, *Zavodsk. laboratoriya*, No. 8-9, **27**, 31 (1932); N. A. Tananaev and I. D. Frolov, *Zh. prikl. khim.*, **7**, No. 4, 609 (1934).
5. Gmelings Handbuch der anorganische Chemie, 8<sup>te</sup> Auflage, system-nummer 27, Teil A, Lief. 2, 1942, s. 355, 357, 361.

6. I. V. Tananaev and N. V. Mzareulishvili, Zh. neorgan. khimii 1, 1826 (1956).
7. A. S. Tikhonov, N. K. Vitchenko, O. D. Talalaeva, and P. I. Yashkova, Zh. neorgan. khimii 2, 2196 (1957).
8. I. V. Tananaev and N. V. Mzareulishvili, Zh. neorgan. khimii 1, 2225 (1956).
9. N. I. Block, Qualitative Analysis [Russian translation] GONTI, Moscow-Leningrad, 1952, p. 191; A Brief Handbook of Chemistry, edited by V. I. Perel'man [in Russian] 3rd ed. GONTI, Moscow, 1954, p. 413.
10. I. V. Tananaev and E. P. Shcheglova, Zh. analit. khimii 12, 671 (1957).
11. I. V. Tananaev and N. V. Mzareulishvili, Zh. neorgan. khimii 1, 2216 (1956).
12. I. V. Tananaev and M. Ya. Bokmel'der, Zh. neorgan. khimii 2, No. 12, 2700 (1957).
13. M. Ya. Bokmel'der, Dissertation [in Russian] Moscow, 1960.
14. I. V. Tananaev and M. I. Levina, Zh. neorgan. khimii 2, 1601 (1957).
15. N. V. Mzareulishvili, Dissertation [in Russian] Tbilisi, 1953.
16. I. V. Tananaev and M. Ya. Bokmel'der, Zhur. neorgan. khimii 3, 1273 (1958).
17. I. V. Tananaev and M. A. Glushkova, Trans. Committee. on Analytical Chemistry [in Russian] Izd. AN SSSR 5, (8) 22 (1954).

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations, as given in the original Russian journal. Some or all of this periodical literature may well be available in English translation. A complete list of the cover-to-cover English translations appears at the back of this issue.

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# THE PEROXIDES OF TITANIUM, ZIRCONIUM, AND CERIUM FORMED IN THE REACTION OF THEIR HYDROXIDES WITH HYDROGEN PEROXIDE

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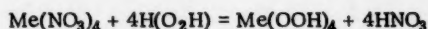
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No. 6, pp. 958-964, June, 1961

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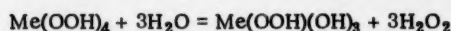
The hydroxides of tetravalent elements,  $Ti^{4+}$ ,  $Zr^{4+}$ ,  $Hf^{4+}$ , and  $Th^{4+}$  possess an unusual property in that they yield specific easily made compounds when they react with hydrogen peroxide. One lanthanide, cerium in the tetravalent state, also undergoes this reaction. The peroxides of cerium resemble in their chemical properties the corresponding derivatives of the titanium subgroup elements.

Several methods of preparing the peroxides of titanium, zirconium, and cerium are discussed in the literature. The peroxides can be prepared by:

1. Treating  $Ti^{4+}$ ,  $Zr^{4+}$ , and  $Ce^{4+}$  salts with solutions of ammonia and hydrogen peroxide [1-6]. On the basis of Colvert's work, where it was shown that hydrogen peroxide acts as a monobasic acid  $H(OOH)$ , Pisarzhevskii proposed the following mechanism for the reaction:

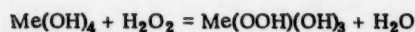


The hydroperoxide  $Me(OOH)_4$  formed in this reaction is a salt of a weak acid and hydrolyzes as shown below,

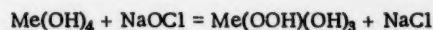


to give a hydroperoxide of the composition  $Me(OOH)(OH)_3$ .

2. The reaction of  $Ti^{4+}$ ,  $Zr^{4+}$ , and  $Ce^{4+}$  hydroxides with hydrogen peroxide [5-7]. Pisarzhevskii represented the reaction by the equation



3. The action of sodium hypochlorite on hydrated oxides (of zirconium, et al.) [6] as shown below,



4. Peroxides of cerium can also be made by the autooxidation of cerium salts [8-9].

Pisarzhevskii [6], Classen [10], Schwarz and Giese [11], Cleve [2], and Bailey [12] represented their peroxides  $Ti^{4+}$ ,  $Zr^{4+}$ , and  $Ce^{4+}$  by the general formula  $MeO_3 \cdot 2H_2O$ . More recently Schwarz and Giese [11], Gantz and Lambert [13], Macrae and Wieland [14, 15], and Lawson and Balson [7] have for very good reasons come to regard the

peroxides of  $Ti^{4+}$ ,  $Zr^{4+}$ , and  $Ce^{4+}$  as derivatives of the type  $Me(OOH)(OH)_3$  or  $\left[ \begin{array}{c} HO \diagup \\ HO \diagdown \end{array} Me \begin{array}{c} \diagup OOH \\ \diagdown OH \end{array} \right]$ , whereas Babko

and Volkova [16, 17] claim that complexes may also be formed with hydrogen peroxide. Schwarz and Giese [11] have done some interesting work in an attempt to find out in what form is the oxygen in the peroxides of cerium and titanium subgroup elements. Using the method developed by Meyer and Pawletta [18] they proved that the active oxygen in their peroxides and related derivatives was not in the form of attached hydrogen peroxide but in the form of an  $-O-O-$  bridge. The peroxides of cerium and titanium subgroup elements, like many other oxidizing

agents, are unstable; on storage they gradually lose the active oxygen and explode when rapidly heated. We would like to mention that the above-mentioned workers used ordinary synthetic methods using hydrogen peroxide of concentrations not in excess of 30%.

## EXPERIMENTAL

In order to determine how the peroxides of titanium, zirconium, and cerium are formed and what type of peroxides result we decided to carry out a systematic investigation of the reactions of the respective hydroxides with hydrogen peroxide over a wide range of concentrations (0–98%) and at two temperatures, 0 and  $-20^{\circ}\text{C}$ . It should

be pointed out that  $\text{Ti}(\text{OH})_4$ ,  $\text{Zr}(\text{OH})_4$ , and  $\text{Ce}(\text{OH})_4$  all are very sparsely soluble (the solubility products are:  $\text{SP}_{\text{Zr}(\text{OH})_4} = 8 \cdot 10^{-12}$  and  $\text{SP}_{\text{Ce}(\text{OH})_4} = 2 \cdot 10^{-48}$  [19]), and consequently one can hardly detect any traces of these compounds in aqueous solutions of hydrogen peroxide. Our method simply involved stirring freshly precipitated hydroxides for a fixed period of time and under isothermal conditions in solutions of hydrogen peroxide until the chemical analysis of the liquid and solid phases (determined graphically from the residue) indicated no more changes in the composition. In this work it is important that only highly active freshly precipitated hydroxides be used, since only then are the peroxides readily formed.

The hydroxide of tetravalent titanium was prepared by precipitating trivalent titanium with ammonium sulfate and simultaneously oxidizing it to the tetravalent state by the oxygen in the air; the oxidation was accompanied by a change in color from dark green to white. After the product was filtered out and thor-

oughly washed it was dried in a vacuum desiccator at  $20^{\circ}$  and ground into a fine powder. The differential heating curves of  $\text{Ti}(\text{OH})_4$  (Fig. 1), recorded on a automatic Kurnakov pyrometer at the heating rate of 3–4 deg/min using a Pt–PtRh thermocouple, show that endothermic changes take place between 120 and  $135^{\circ}$  and between 290 and  $407^{\circ}\text{C}$  attributed to the dehydration of the product. The chemical analysis also involved a determination of active oxygen by a titration with 0.1 N  $\text{KMnO}_4$  in sulfuric acid. The titanium in the solid residue was determined gravimetrically in the form of  $\text{TiO}_2$  fired at  $800\text{--}900^{\circ}\text{C}$ .

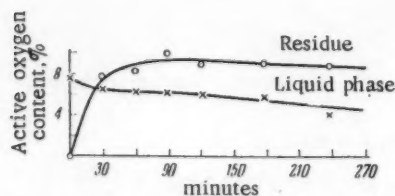


Fig. 2. The equilibration time in the system  $\text{Ti}(\text{OH})_4\text{--H}_2\text{O}_2\text{--H}_2\text{O}$  at  $0^{\circ}$ .

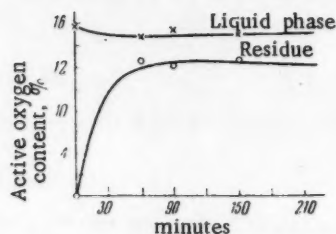


Fig. 3. The equilibration time in the system  $\text{Ti}(\text{OH})_4\text{--H}_2\text{O}_2\text{--H}_2\text{O}$  at  $-20^{\circ}$ .

Results obtained at 0 and  $-20^{\circ}\text{C}$ . As we have already mentioned the equilibration time in the reaction of titanium hydroxide with hydrogen peroxide was determined analytically by noting when the active oxygen content of the liquid and solid phases as well as the overall composition of the solid product became constant. The curves in Fig. 2 and 3 (0 and  $-20^{\circ}$  plots) clearly indicate that a time interval of 60–90 min is sufficient for attaining the desired equilibrium. The reaction of  $\text{Ti}(\text{OH})_4$  with  $\text{H}_2\text{O}_2$  at  $0^{\circ}\text{C}$  was investigated over a range of hydrogen peroxide concentrations from 7.18 to 91.76% (in the liquid phase) and interpreted as the formation of solid phases in the ternary system  $\text{Ti}(\text{OH})_4\text{--H}_2\text{O}_2\text{--H}_2\text{O}$ . The results are presented in Table 1 and Fig. 4.

At hydrogen peroxide concentrations in the range from 7.18 to 46.83% we detected the formation of one solid phase; it was a lemon-colored peroxide compound of the composition  $\text{TiO}_3 \cdot 2\text{H}_2\text{O}$ . When the concentration of hydrogen peroxide in the liquid phase exceeds 50% the "residues" begin to decompose.

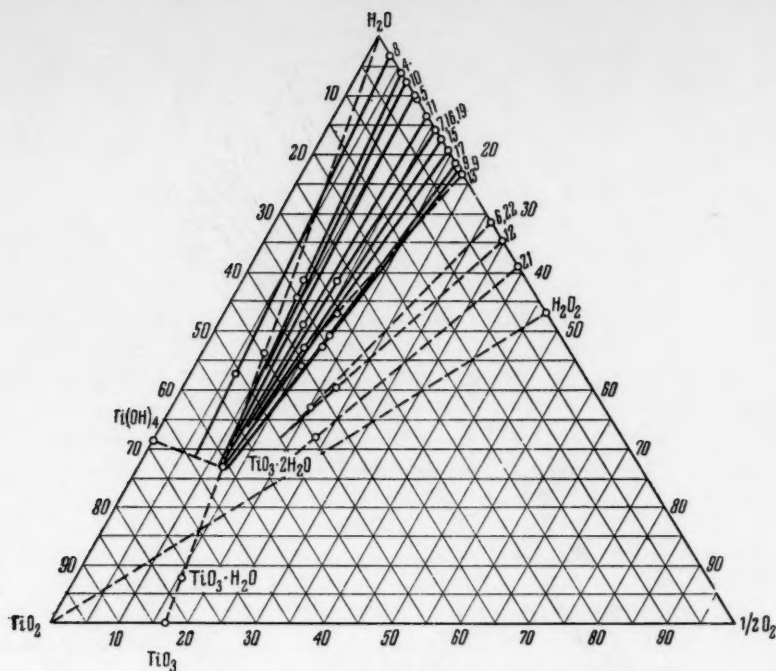


Fig. 4. The 0° isotherm for the system  $\text{Ti(OH)}_4\text{-H}_2\text{O}_2\text{-H}_2\text{O}$ .

TABLE 1. Experimental Data from the Reaction of  $\text{Ti(OH)}_4$  with  $\text{H}_2\text{O}_2$  Solutions at 0°

Expt. No.	Liq. phase compn., wt. %		Solid residue compn., wt. %		Solid phase.
	Act. $\text{C}_2$	$\text{H}_2\text{O}_2$	Act. $\text{O}_2$	$\text{TiO}_3$	
8	3,38	7,18	6,80	50,40	$\text{Ti(OH)}_4 + \text{TiO}_3 \cdot 2\text{H}_2\text{O}$
4	6,28	13,35	8,84	32,12	$\text{TiO}_3 \cdot 2\text{H}_2\text{O}$
10	7,99	16,99	9,09	34,66	Ditto
5	10,03	21,30	9,55	46,25	» »
18	10,62	22,58	9,97	40,00	» »
11	13,56	28,82	12,33	36,50	» »
16	15,77	33,52	13,69	27,47	» »
7	15,77	33,52	14,47	25,75	» »
19	15,87	33,74	13,02	39,54	» »
15	17,56	37,33	15,85	40,56	» »
17	19,41	41,26	14,41	38,18	» »
9	21,14	44,94	17,05	33,92	» »
19	22,03	46,83	16,73	35,21	» »
13	23,53	50,02	16,66	30,61	Decomposed
6	31,40	66,75	20,29	42,82	»
22 res.	34,58	73,52	22,14	42,19	»
12	34,91	74,22	23,21	37,03	»
21 res.	39,33	83,61	23,27	45,62	»
20 res.	43,16	91,76	26,86	38,00	Freezing with the formation of solid $\text{H}_2\text{O}_2$

A parallel investigation at  $-20^\circ$  over a hydrogen peroxide (liquid phase) concentration range from 21.68 to 95.22% (Table 2 and Fig. 5) contributed nothing really new as far as discovery of other peroxides is concerned since the compound  $\text{TiO}_3 \cdot 2\text{H}_2\text{O}$  had already been found. The compound of the composition  $\text{TiO}_3 \cdot 2\text{H}_2\text{O}$  should be written in the form  $\text{Ti(OOH)(OH)}_3$ , since it can be regarded as a derivative of  $\text{Ti(OH)}_4$  with one hydroxyl group replaced by a perhydroxyl (OOH) group. The nature of the compound was deduced from subsequent work in which the specific properties of this peroxide were investigated during dehydration and thermal decomposition. In fact, if we take the entire solid residue of the composition  $\text{TiO}_3 \cdot 2\text{H}_2\text{O}$  and wash it with ethanol and ether we get a product

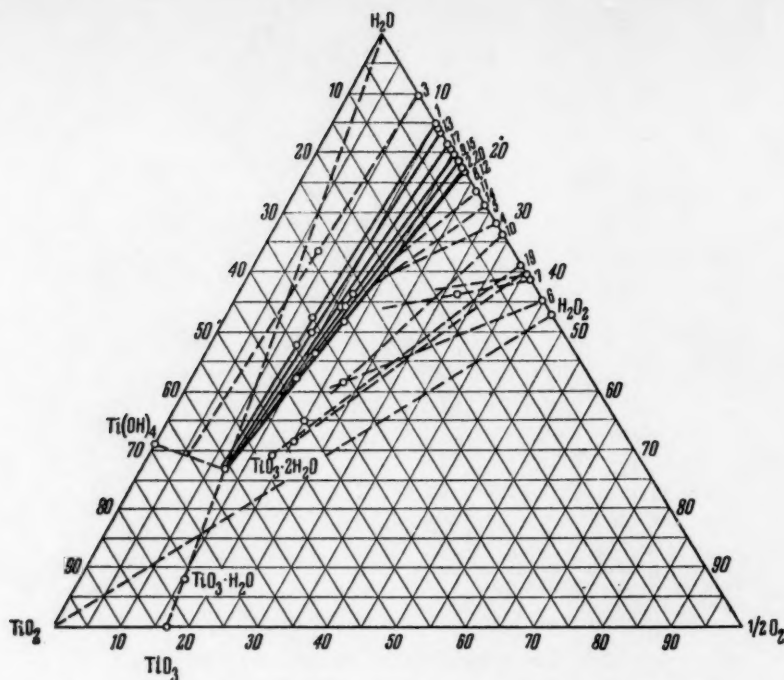


Fig. 5. The  $-20^{\circ}$  isotherm for the ternary system  $\text{Ti}(\text{OH})_4\text{-H}_2\text{O}_2\text{-H}_2\text{O}$ .

TABLE 2. Experimental Data from the Reaction  $\text{Ti}(\text{OH})_4$  with  $\text{H}_2\text{O}_2$  Solutions at  $-20^{\circ}$

Expt. No.	Liq. cmpn., wt. %		Solid residue cmpn., wt. %		Solid phase
	Act. $\text{O}_2$	$\text{H}_2\text{O}_2$	Act. $\text{O}_2$	$\text{TiO}_2$	
3	10,02	21,68	8,19	28,01	Ice- $\text{TiO}_3\cdot 2\text{H}_2\text{O}$
17	14,28	30,36	11,54	36,58	
1	15,03	31,95	12,88	35,00	Ditto
15	19,52	41,49	14,69	39,10	" "
9	20,02	42,56	16,45	29,08	" "
2	21,12	44,90	15,71	30,06	" "
12	22,56	47,96	14,28	42,28	" "
8	22,64	48,13	17,40	30,69	" "
11	22,90	48,70	15,43	37,78	" "
20	25,81	54,87	16,15	34,78	Decomposed
14	26,25	55,80	17,93	26,03	
5	28,40	60,37	25,26	8,90	"
4	31,50	66,97	27,82	14,72	"
10	33,30	70,79	22,54	36,59	"
18 res.	33,92	72,11	20,03	48,03	"
19 res.	38,30	81,42	17,99	52,98	"
7	40,44	85,97	31,40	11,61	"
6	44,79	95,22	37,93	10,61	"

which analyzes:  $\text{O}_2$  act. = 9,71%,  $\text{TiO}_2$  = 63,23%;  $\text{H}_2\text{O}$  = 27,06%. Calculated for  $\text{TiO}_3\cdot 2\text{H}_2\text{O}$ :  $\text{O}_2$  act. = 12,13%;  $\text{TiO}_2$  = 60,58%;  $\text{H}_2\text{O}$  = 27,29%. The differential heating curve (Fig. 6) of a product thus treated indicated an exothermic process at temperatures between 23 and  $70^{\circ}$  and an endothermic at  $105^{\circ}$ . The first (exothermic) process represents the decomposition of  $\text{Ti}(\text{OOH})(\text{OH})_3$ , and the accompanying evolution of oxygen, the second (endothermic) process is connected with the first dehydration stage of the newly formed  $\text{Ti}(\text{OH})_4$ . The  $\text{Ti}(\text{OOH})(\text{OH})_3$  structure for the titanium peroxide is supported by a number of workers [6, 7, 13, 14, et al.] and appears most plausible.

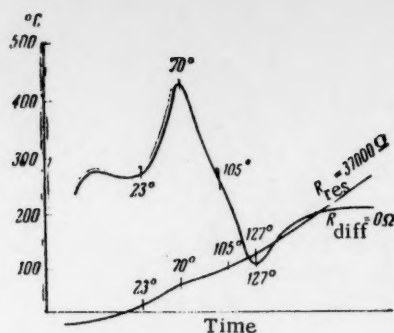


Fig. 6. The differential heating curve of a titanium peroxide with an approximate composition of  $\text{TiO}_3 \cdot 2\text{H}_2\text{O}$ .

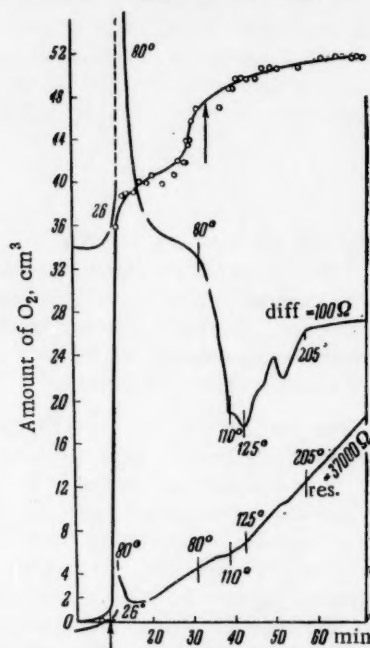


Fig. 7. The differential heating curve of the solid residue of the composition  $\text{TiO}_3 \cdot 2\text{H}_2\text{O}$ .

If this compound retains excess hydrogen peroxide the exothermic decomposition becomes more pronounced (Fig. 7) and the evolution of active oxygen proceeds in two stages: from the decomposition of  $\text{H}_2\text{O}_2$  and of  $\text{Ti}(\text{OOH})(\text{OH})_3$ . In Fig. 7 we have recorded the differential heating curve simultaneously with the amount of oxygen evolved during the thermal decomposition.

## SUMMARY

1. An investigation of the reaction of  $\text{Ti}(\text{OH})_4$  with  $\text{H}_2\text{O}_2$  at  $0^\circ$  and  $-20^\circ\text{C}$  and over a wide range of  $\text{H}_2\text{O}_2$  concentrations revealed the formation of only one peroxide phase of the general composition  $\text{TiO}_3 \cdot 2\text{H}_2\text{O}$ .

2. Dehydration experiments and differential heating curves accompanied by a plot of the oxygen evolved during the thermal decomposition enabled us to conclude that the discovered compound is of the type  $\text{Ti}(\text{OOH})(\text{OH})_3$ .

## LITERATURE CITED

1. R. Hermann, J. prakt. Chem. (1) 30, 184 (1843).
2. M. P. T. Cléve, Bull. Soc. chim. France N 2, 43, 57 (1885).
3. L. de Boibaudran, Compt. rend. 100, 605 (1885).
4. G. H. Bailey, Jahresber. (2), 1886, 1941.
5. M. P. T. Cléve, Jahresber. 1885, 491.
6. L. P. Pisarzhevskii, Zh. russk. fiz.-khim. o-va, 32, 609 (1900).
7. A. Lawson and E. Balson, J. Chem. Soc. 1935, 362.
8. A. Job, Annal. Chim. (7) 20, 253 (1900), Compt. rend. 126, 246 (1898); Compt. rend. 128, 178 (1899); Compt. rend. 134, 105 (1902); Compt. rend. 36, 45 (1903).
9. E. Bauer, Z. anorgan. und allgem. Chem. 30, 251 (1902).
10. H. Classen, Ber. 21, 370 (1888).
11. R. Schwarz and H. Giese, Z. anorgan. und allgem. Chem. 176, 209 (1928).
12. G. H. Bailey, Jahresber. 1889, 115.
13. D. Gantz and L. Lambert, J. Phys. Chem. 61, N 1, 112 (1957).
14. T. Macrae and H. Wieland, Ann. 483, 229 (1930).
15. H. Wieland and B. Rosenfeld, Ann. 477, 72 (1930).
16. A. K. Babko and A. I. Volkova, Ukr. khim. zh. 20, No. 2, 211 (1954).
17. A. I. Volkova, Dissertation [in Russian] Kiev, 1951.
18. J. Meyer and A. Pawletta, Z. phys. Chem. 125, 66 (1927).
19. I. M. Korenman, Zh. Obshch. khim. 25, 1441 (1950).

All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. Some or all of this periodical literature may well be available in English translation. A complete list of the cover-to-cover English translations appears at the back of this issue.



# THE VIBRATION SPECTRA AND STRUCTURES OF SOME RARE EARTH ELEMENT SILICATES

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We have shown previously [1-3] that investigation of silicate vibration spectra makes it possible to estimate the "degree of polymerization" of the silicon-oxygen tetrahedra and the shape of the complex anions formed by them. The object of the present paper was to apply these methods to a study of the structure of rare earth element silicates, of composition  $R_2O_3 \cdot SiO_2$ ,  $2R_2O_3 \cdot 3SiO_2$ , and  $R_2O_3 \cdot 2SiO_2$ , corresponding (as regards Si and O content) to oxyorthosilicate, orthosilicate, and pyrosilicate. At the same time, determination of their crystal structures, or at least of the structures of the complex anions of these substances, may be of interest for the crystal chemistry of silicates and for the study of the electronic structure of rare earth ions in crystals.

## EXPERIMENTAL

All the silicates which we investigated were synthesized by Bondar\*, Galakhov, and Leonov [4, 5]. The uniformity of our samples was checked by microscopic and x-ray phase analysis. The samples for investigation of their infrared spectra were prepared in the form of discs, pressed from a mixture of the material in question with potassium bromide, or in the form of finely dispersed suspensions of the material in paraffin oil.\* Practically identical spectra were obtained by both methods. The spectra were recorded using a VIKS-M3 vacuum spectrometer with an NaCl prism, an ISP-14b spectrometer with a KBr prism, and, in some cases, and IKS-14 double beam spectrometer.

Figure 1 and 2 show the absorption spectra of Y, Gd, and Sm silicates, of compositions  $R_2O_3 \cdot SiO_2$  and  $2R_2O_3 \cdot 3SiO_2$ . The spectra show a strong absorption region  $850-1050\text{ cm}^{-1}$ , where in most cases there are three strong bands, which, in turn, often have a doublet structure. There is another group of bands in the region below  $600\text{ cm}^{-1}$ . The absence of absorption in the  $600-750\text{ cm}^{-1}$  region, characteristic of silicates containing complex anions with  $SiO_4$  tetrahedra combined with common oxygen atoms [1-3], agrees with the view that there are isolated  $[SiO_4]^{4-}$  ions in these compounds, and suggests that their structural formulae may be written  $R_2(SiO_4)O$  and  $R_4(SiO_4)_3$ . The three intense bands in the  $850-1050\text{ cm}^{-1}$  region may be attributed to the triply degenerate valency vibrations of the  $SiO_4$  group ( $F_2$ ). The appearance of three bands is evidently associated with the observed degeneracy under the influence of the internal field of the crystal.\*\* The often observed doublet structure of these bands is probably due to splitting of the internal vibrations of the complex ions as the result of interaction between the ions in the crystal lattice [7]. The other, type  $A_1$ , valency vibration of the  $SiO_4$  ion, of frequency  $\sim 775\text{ cm}^{-1}$ , is not usually observed in the absorption spectrum. The frequencies of the Si-O deformation vibrations and of the metal-oxygen vibrations are in the region below  $600\text{ cm}^{-1}$ . It should be noted that the comparison of the pyrosilicate spectra (see below) with these of the orthosilicates indicates that the latter are unstable. The orthosilicate spectra often show bands corresponding to pyrosilicates (Table 1). It is characteristic that spectra recorded immediately after synthesis of the orthosilicates did not show pyrosilicate absorption. After some time, the spectra of all the samples showed  $Si_2O_7$  ion bands (Fig. 2),\*\*\* indicating that pyrosilicate is one of the main decomposition products.

The most detailed investigation spectra was made with compounds of the composition  $R_2O_3 \cdot 2SiO_2$ , with the cations: Sc, Y, La, Ce, Sm, Gd, Dy, Er, Yb. These compounds could be divided into three groups according to their

\* Absorption by the immersion medium is excluded from the figure shown in this paper.

\*\* The observation that  $F_2$  type vibrations of the  $SiO_4$  ion are split up into three components indicates that the position symmetry of these ions in the lattice (site-symmetry [6]) is not higher than  $C_{2v}$ , or indeed simple  $C_1$ .

\*\*\* It cannot be excluded that some of the bands in the  $800-1100\text{ cm}^{-1}$  region may be associated with overtones or combination frequencies, whose intensities are increased by Fermi resonance.

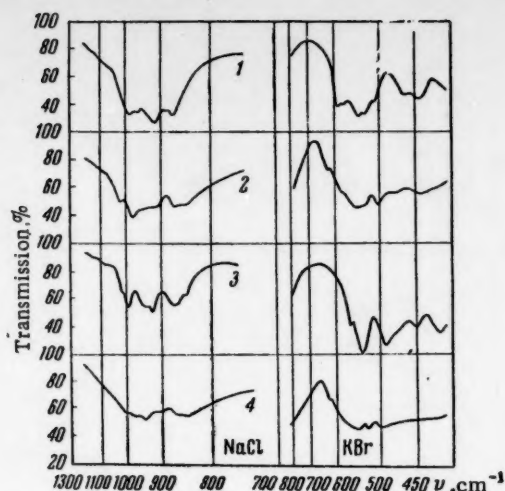


Fig. 1. Infrared spectra of Y and Gd silicates containing  $\text{SiO}_4$  ions: 1)  $\text{Y}_2(\text{SiO}_4)\text{O}$  in paraffin oil; 2)  $\text{Y}_4(\text{SiO}_4)_3$  pressed with KBr (5 mg to 2 g KBr); 3)  $\text{Gd}_2(\text{SiO}_4)\text{O}$  in paraffin oil; 4)  $\text{Gd}_4(\text{SiO}_4)_3$  pressed with KBr (5 mg to 2 g KBr).

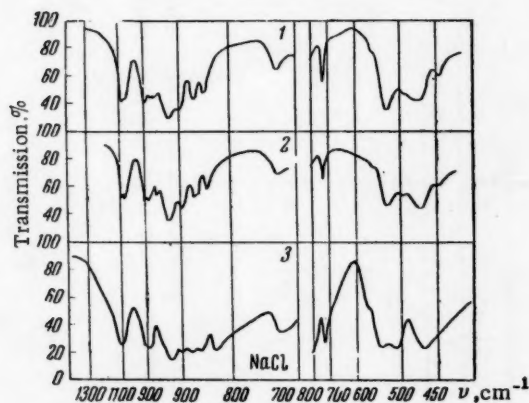


Fig. 3. Infrared spectra of the silicates of La, Ce, and Sm with  $\text{Si}_2\text{O}_7$  ions: 1)  $\text{La}_2(\text{Si}_2\text{O}_7)$  in paraffin oil; 2)  $\text{Ce}_2(\text{Si}_2\text{O}_7)$  in paraffin oil; 3)  $\text{Sm}_2(\text{Si}_2\text{O}_7)$  pressed with KBr (10 mg to 2 g KBr).

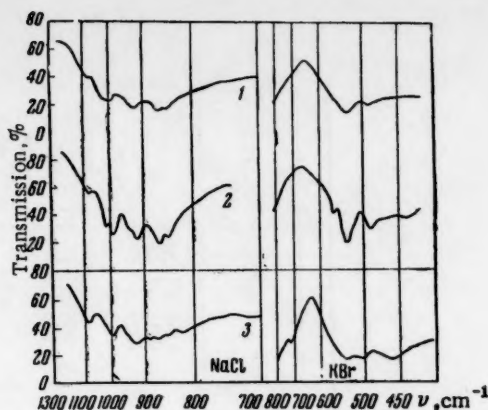


Fig. 2. Infrared spectra of Sm silicates containing  $\text{SiO}_4$  ions: 1)  $\text{Sm}_2(\text{SiO}_4)\text{O}$  pressed with KBr (10 mg to 2 g KBr); 2)  $\text{Sm}_4(\text{SiO}_4)_3$ , 1 day after synthesis, pressed with KBr (5 mg to 2 g KBr); 3)  $\text{Sm}_4(\text{SiO}_4)_3$ , three weeks after synthesis, pressed with KBr (10 mg to 2 g KBr).

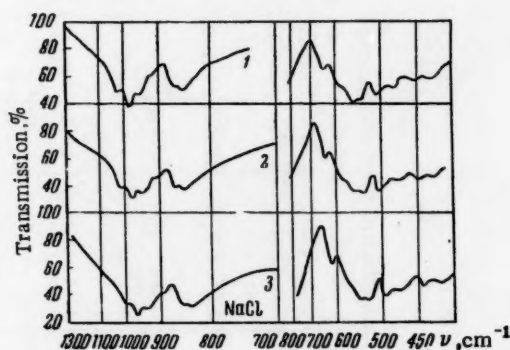
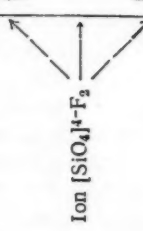


Fig. 4. Infrared spectra of the silicates of Y, Gd, and Dy with  $\text{Si}_2\text{O}_7$  ions: 1)  $\text{Y}_2(\text{Si}_2\text{O}_7)$  pressed with KBr (5 mg to 2 g KBr); 2)  $\text{Gd}_2(\text{Si}_2\text{O}_7)$  pressed with KBr (10 mg to 2 g KBr); 3)  $\text{Dy}_2(\text{Si}_2\text{O}_7)$  pressed with KBr (10 mg to 2 g KBr).

spectra; there was very little difference between the spectra within each group. The first group comprised the silicates of La, Ce, and Sm (Fig. 3). These showed a set of seven bands in the  $800\text{--}1100\text{ cm}^{-1}$  region; some of the bands showed a definite doublet structure. There was a second set of strong bands in the region below  $600\text{--}550\text{ cm}^{-1}$ , and, finally, all three compounds showed a single band at close to  $725\text{ cm}^{-1}$ . The second group comprised the silicates of Y, Gd, and Dy (Fig. 4). These showed six bands in the  $850\text{--}1050\text{ cm}^{-1}$  region, none of them showing any doublet structure. Besides the bands below  $600\text{ cm}^{-1}$ , there was also a single band at about  $630\text{ cm}^{-1}$ . The third group, comprising the silicates of Sc, Er, and Yb, showed the simplest spectra (Fig. 5). There were four bands in the  $850\text{--}1150\text{ cm}^{-1}$  region, of which one was usually double, a number of bands below  $600\text{ cm}^{-1}$ , and no band in the  $600\text{--}850\text{ cm}^{-1}$  region.

TABLE 1. Infrared Spectra of Rare Earth Metal Oxyorthosilicates and Orthosilicates

Frequency attribution	Frequencies in infrared absorption				
	Sm <sub>2</sub> (SiO <sub>3</sub> )O	Sm <sub>4</sub> (SiO <sub>3</sub> ) <sub>2</sub>		Y <sub>2</sub> (SiO <sub>3</sub> )O	Gd <sub>2</sub> (SiO <sub>3</sub> )O
		1 day after synthesis	3 weeks after synthesis		
Ion [SiO <sub>4</sub> ] <sup>4-</sup> -F <sub>2</sub>  A <sub>1</sub> (H <sub>2</sub> O)	1072* c.t. { 1043 c. 992 o. c. }	1082* cp. { 1015 c. 990 o. c. }	1092* c. 995 o. c.	1153 o. c.t. 1083* o. c.t. { 993 o. c. 984 c. }	1159 o. c.t. 1074* o. c.t. { 1023 c. 999 o. c. }
	318 o. c. — { 866 o. c. 847 c. }	942 c. { 920 o. c. — }	955 cp. { 928 o. c. 893* c. 875* c. }	918 o. c. — { 892 c. 843 o. c. }	946 o. c. { 929 o. c. — }
	—	867 o. c. { 849 c. — }	858 c. { 828 c. — }	872 o. c. { 857* c. — }	865 c. { 851 cp. — }
Ion [Si <sub>2</sub> O <sub>7</sub> ] <sup>6-</sup> (impurity)	—	—	—	—	—
Si-O deformation and M-O vibration	554 cp. 532 o. c. 492 c.	564 cp. 533 o. c. 492 c. 472 c.t. 447 cp.	544 o. c. 508 o. c. 466 c.	597 o. c. 583 c. 547 o. c. 532 o. c. 513 c. 466 cp. 448 cp.	590 c. 554 o. c. 536 c. 510 o. c. 481 cp. 448 cp.
				566 c. 540 o. c. 525 o. c. 501 c.	548 o. c. 525 o. c. 501 c.

Notes: The bands marked with an asterisk are probably associated with the impurity ion [Si<sub>2</sub>O<sub>7</sub>]<sup>6-</sup>. The meanings of the abbreviations in Tables 1-3 are: (na) nonactive in infrared vibration spectrum; o. c.t. very weak; cp. medium; c. strong; o. c. very strong.



Thus, even a preliminary consideration of the  $R_2O_3 \cdot 2SiO_2$  silicate spectra indicates the existence of three different structural types. In this there is a curious reverse periodicity. The silicates of the elements immediately following La repeat the structure of La silicate; the following group of silicates (Gd, Dy) crystallizes with the structure of Y silicate; the silicates of the elements completing the lanthanide group (Er, Yb) coincide in structure with Sc silicate.

### Discussion of Experimental Results

As previously [1-3], in interpreting the results obtained, we consider the valency vibrations of the metal-oxygen polyhedra can be neglected to a first approximation. This is evidently correct for silicates with cations whose bonds with oxygen are only covalent to a negligible extent, or which have such a high mass that the frequency of the M-O vibrations is low. It is not immediately obvious that this treatment is applicable to the spectra of the rare earth element silicates. However, the M-O vibration frequencies in the spectra of the ortho- and oxyorthosilicate do not in any case exceed  $\sim 550 \text{ cm}^{-1}$ , and this indicates that it is permissible to consider separately the valency vibrations of the anions. Such a clear interpretation would not be possible if the Si-O deformation frequencies were of the same order as the M-O frequencies.

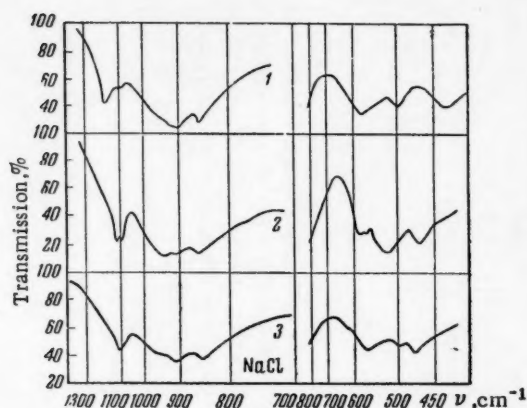


Fig. 5. Infrared spectra of the silicates of Sc, Er, and Yb with a thortveitite structure: 1)  $Sc_2(Si_2O_7)$  (synthetic) pressed with KBr (5 mg to 2 g KBr); 2)  $Er_2(Si_2O_7)$  pressed with KBr (10 mg to 2 g KBr); 3)  $Yb_2(Si_2O_7)$  pressed with KBr (10 mg to 2 g KBr).

reaction between the ions in the lattice, will, in accordance with Davydov's theory [7], be shown preferentially by the vibrations with the highest dipole moment. It should be noted that  $A_2$  type vibrations, with  $C_{2v}$  symmetry of the  $Si_2O_7$  ion, are nonactive in the absorption spectrum; their appearance in the infrared spectra indicates that the  $Si_2O_7$  ion has lower symmetry, or that these ions occupy positions with site-symmetry below  $C_{2v}$  ( $C_2$ ,  $C_3$  or  $C_1$ ). The single medium intensity band at  $\sim 730 \text{ cm}^{-1}$  is attributed to one of the components (the low frequency one) into which the pulsation frequency of the  $SiO_4$  group and  $Si_2O_7$  ion is split up. Using the connection between the value of the tetrahedral pulsating frequency splitting (and, consequently, the position of the band in question) and the value of the SiOSi angle in the  $Si_2O_7$  group [2], we may conclude that this group is sharply bent in shape (the SiOSi angle  $\leq 120^\circ$ ).

The Y, Gd, and Dy pyrosilicate spectra contain six intense bands in the  $850\text{--}1025 \text{ cm}^{-1}$  range, which indicates that it is correct to select  $C_{2v}$  symmetry for the  $Si_2O_7$  ion. These ions probably occupy positions with  $C_{2v}$  site-symmetry in the lattice, since with a lower symmetry, the  $A_2$  type vibration of the ion would change so as to be forbidden in the infrared spectrum. The bands at  $630 \text{ cm}^{-1}$ , corresponds to the  $730 \text{ cm}^{-1}$  vibrations of the La, Ce, and Sm silicates, which indicates an increase in the SiOSi angle to about  $160^\circ$ .

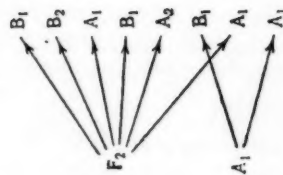
The spectra of the Er and Yb pyrosilicates, and the very similar Sc pyrosilicate \* spectrum, differ in having

\* We have recorded the spectrum of natural thortveitite, as well as that of synthetic  $Sc_2Si_2O_7$ , and the results are identical.

We have shown [1] that association of  $SiO_4$  tetrahedra into a "double"  $Si_2O_7$  group leads to a splitting of the valency vibrations of the  $SiO_4$  tetrahedron, in accordance with the scheme on the left hand side of Table 2. There is particularly strong splitting of the fully symmetrical (pulsation) vibrations of the tetrahedron, so that one of the two components falls in the frequency region of the triply degenerate tetrahedral vibration, and its identification is generally difficult. The other component falls in the  $600\text{--}700 \text{ cm}^{-1}$  range, which is free from bands in the orthosilicate spectrum, and may be used to indicate the presence of  $Si_2O_7$  groups. The position of the band (i.e., the value of the splitting) depends on the size of the SiOSi angle, and may be used for its approximate evaluation.

Taking the above into account, we will now attempt an interpretation of the spectra. As already stated, the spectra of the La, Ce, and Sm silicates contain seven bands in the  $800\text{--}1100 \text{ cm}^{-1}$  region, some of which show a doublet structure. These bands may be considered as seven normal vibrations of the  $Si_2O_7$  ion in this region of the spectrum. In comparing the frequencies in Table 2, we also make use of the circumstance that a doublet structure, produced by inter-

TABLE 2. Frequencies in the Infrared Spectra of the Pyrosilicates of Rare Earth Metals

Frequency attribution		Frequencies in Infrared spectra						
$[\text{SiO}_4]^{4-}(\text{Td}) \rightarrow [\text{Si}_2\text{O}_7]^{6-}(\text{C}_{2v})$		$\text{La}_2(\text{Si}_2\text{O}_7)$	$\text{Ce}_2(\text{Si}_2\text{O}_7)$	$\text{Sm}_2(\text{Si}_2\text{O}_7)$	$\text{Y}_2(\text{Si}_2\text{O}_7)$	$\text{Gd}_2(\text{Si}_2\text{O}_7)$	$\text{Dy}_2(\text{Si}_2\text{O}_7)$	
		$\left\{ \begin{array}{l} 1085 \text{ o. c.} \\ 1070 \text{ o. c.} \\ 996 \text{ o. c.} \\ 978 \text{ c.} \\ 964 \text{ c.} \end{array} \right.$	$\left\{ \begin{array}{l} 1094 \text{ o. c.} \\ 1076 \text{ o. c.} \\ 1000 \text{ o. c.} \\ 987 \text{ o. c.} \\ 960 \text{ c.} \end{array} \right.$	$\left\{ \begin{array}{l} 1103 \text{ o. c.} \\ 1094 \text{ o. c.} \\ 1005 \text{ o. c.} \\ 995 \text{ o. c.} \\ 955 \text{ c.} \end{array} \right.$	$\left\{ \begin{array}{l} 1024 \text{ c.} \\ 982 \text{ o. c.} \\ 954 \text{ c.} \\ 915 \text{ cp.} \end{array} \right.$	$\left\{ \begin{array}{l} 1015 \text{ c.} \\ 979 \text{ o. c.} \\ 950 \text{ c.} \\ 914 \text{ cp.} \end{array} \right.$ $A_2 \text{ nonactive ?}$	$\left\{ \begin{array}{l} 1023 \text{ c.} \\ 982 \text{ o. c.} \\ 953 \text{ c.} \\ 911 \text{ cp.} \\ 866 \text{ c.} \\ 846 \text{ c.} \end{array} \right.$	
		$\left\{ \begin{array}{l} 926 \text{ o. c.} \\ 900 \text{ c.} \\ 864 \text{ o. c.} \\ 844 \text{ c.} \end{array} \right.$	$\left\{ \begin{array}{l} 928 \text{ o. c.} \\ 897 \text{ o. c.} \\ 868 \text{ o. c.} \\ 862 \text{ c.} \\ 840 \text{ c.} \end{array} \right.$	$\left\{ \begin{array}{l} 930 \text{ o. c.} \\ 900 \text{ c.} \\ 878 \text{ c.} \\ 859 \text{ c.} \\ 830 \text{ o. c.} \end{array} \right.$	$\left\{ \begin{array}{l} 870 \text{ c.} \\ 850 \text{ c.} \end{array} \right.$	$\left\{ \begin{array}{l} 867 \text{ c.} \\ 850 \text{ c.} \end{array} \right.$	$\left\{ \begin{array}{l} 866 \text{ c.} \\ 846 \text{ c.} \end{array} \right.$	
		728 cp.	730 cp.	725 cp.	635 cp.	627 cp.	631 cp.	
Si-O deformation and M-O vibration		$\left\{ \begin{array}{l} 558 \text{ cp.} \\ 526 \text{ o. c.} \\ 496 \text{ c.} \\ 474 \text{ o. c.} \\ 448 \text{ cp.} \end{array} \right.$	$\left\{ \begin{array}{l} 558 \text{ c.} \\ 526 \text{ o. c.} \\ 500 \text{ cp.} \\ 472 \text{ o. c.} \\ 448 \text{ c.} \end{array} \right.$	$\left\{ \begin{array}{l} 567 \text{ cp.} \\ 540 \text{ o. c.} \\ 511 \text{ o. c.} \\ 466 \text{ o. c.} \\ - \end{array} \right.$	$\left\{ \begin{array}{l} 587 \text{ cp.} \\ 555 \text{ o. c.} \\ 541 \text{ c.} \\ 508 \text{ o. c.} \\ 481 \text{ c.} \\ 452 \text{ cp.} \\ 432 \text{ cp.} \end{array} \right.$	$\left\{ \begin{array}{l} 576 \text{ cp.} \\ 545 \text{ o. c.} \\ 529 \text{ o. c.} \\ 501 \text{ o. c.} \\ 472 \text{ cp.} \\ 445 \text{ cp.} \\ 429 \text{ cp.} \end{array} \right.$	$\left\{ \begin{array}{l} 583 \text{ c.} \\ 554 \text{ o. c.} \\ 537 \text{ o. c.} \\ 504 \text{ o. c.} \\ 480 \text{ c.} \\ 449 \text{ cp.} \\ 430 \text{ cp.} \end{array} \right.$	

Notes: In the spectra of the Y, Gd, and Dy silicates, where the SiOSi angle in the Si<sub>2</sub>O<sub>7</sub> groups is higher, the B<sub>1</sub> type vibration frequencies, which arise as the result of splitting of the A<sub>1</sub> type vibrations of SiO<sub>4</sub> tetrahedra, should increase; this is probably responsible for one of the bands in the 900-950 cm<sup>-1</sup> region, but it should be noted that strong interaction between similar type vibrations in frequency B<sub>1</sub> to a considerable extent compels us to assume formal separation of this type of symmetry vibration, produced by splitting of the F<sub>2</sub> and A<sub>1</sub> type vibrations of the SiO<sub>4</sub> group.

TABLE 3. Frequencies in the Infrared Spectra of Rare Earth Metal Pyrosilicates with a Thortveitite Structure

Interpretation				Frequencies in absorption spectra		
Ion [SiO <sub>4</sub> ] <sup>4-</sup> (T <sub>d</sub> symm.)	Ion [Si <sub>2</sub> O <sub>7</sub> ] <sup>6-</sup> (D <sub>3d</sub> symm.)	Site-group C <sub>2h</sub>	Crystal space group C <sub>2h</sub> <sup>3</sup>	Sc <sub>2</sub> Si <sub>2</sub> O <sub>7</sub>	Er <sub>2</sub> Si <sub>2</sub> O <sub>7</sub>	Yb <sub>2</sub> Si <sub>2</sub> O <sub>7</sub>
	A <sub>2d</sub>	B <sub>u</sub>	$\begin{Bmatrix} B_u \\ A_u \end{Bmatrix}$	$\begin{Bmatrix} 1169 \text{ o. c.} \\ 1100 \text{ cp.} \end{Bmatrix}$	$\begin{Bmatrix} 1119 \text{ o. c.} \\ 1095 \text{ o. c.} \end{Bmatrix}$	$\begin{Bmatrix} 1100 \text{ o. c.} \end{Bmatrix}$
	E <sub>g</sub> (na)	$\begin{Bmatrix} B_g (na) \\ A_g (na) \end{Bmatrix}$	$\begin{Bmatrix} B_g (na) \\ A_g (na) \end{Bmatrix}$	—	—	—
	A <sub>1g</sub> (na)	B <sub>u</sub>	$\begin{Bmatrix} B_u \\ A_u \end{Bmatrix}$	$\begin{Bmatrix} 975 \text{ cp.} \\ 907 \text{ o. c.} \end{Bmatrix}$	$\begin{Bmatrix} 943 \text{ o. c.} \\ 915 \text{ o. c.} \end{Bmatrix}$	$\begin{Bmatrix} 955 \text{ o. c.} \\ 915 \text{ o. c.} \end{Bmatrix}$
	A <sub>1g</sub> (na)	A <sub>u</sub>	$\begin{Bmatrix} B_u \\ A_u \end{Bmatrix}$	$\begin{Bmatrix} 852 \text{ o. c.} \end{Bmatrix}$	$\begin{Bmatrix} 858 \text{ o. c.} \end{Bmatrix}$	$\begin{Bmatrix} 852 \text{ o. c.} \end{Bmatrix}$
	A <sub>1g</sub> (na)	A <sub>g</sub> (na)	$\begin{Bmatrix} B_g (na) \\ A_g (na) \end{Bmatrix}$	—	—	—
	A <sub>1g</sub> (na)	A <sub>g</sub> (na)	$\begin{Bmatrix} B_g (na) \\ A_g (na) \end{Bmatrix}$	—	—	$\begin{Bmatrix} 621 \text{ o. c. l. (?)} \end{Bmatrix}$
	Si-O deformation and M-O vibration			$\begin{Bmatrix} 548 \text{ o. c.} \\ 498 \text{ c.} \\ 434 \text{ c.} \end{Bmatrix}$	$\begin{Bmatrix} 588 \text{ c.} \\ 570 \text{ cp.} \\ 542 \text{ cp.} \\ 523 \text{ o. c.} \\ 470 \text{ o. c.} \end{Bmatrix}$	$\begin{Bmatrix} 566 \text{ o. c.} \\ 546 \text{ cp.} \\ 498 \text{ cp.} \\ 476 \text{ o. c.} \end{Bmatrix}$

\* Abbreviations — see Table 1. Notes — see notes to Table 2.

a small number of bands in the Si-O valency vibration region. It is helpful to use the x-ray analysis data for thortveitite [8] in the interpretation of these spectra. The [Si<sub>2</sub>O<sub>7</sub>]<sup>6-</sup> ions in this crystal show D<sub>3d</sub> symmetry (the SiOSi angle = 180°), and this leads to an alternative prohibition in the selection rules for vibrations of the isolated ion. Of the six Si-O valency vibrations, only three can be observed in the infrared spectrum, and the other three must be inactive. One of the frequencies inactive in the absorption spectrum is at ~600-700 cm<sup>-1</sup> (type A<sub>1g</sub>), characteristic of pyrosilicates. The Si<sub>2</sub>O<sub>7</sub> ions in the thortveitite lattice occupy positions with C<sub>2h</sub> site-symmetry. Thus the change from the spectrum of an isolated ion to that of its vibrations in a crystal field must be achieved by the break down of the irreducible representations of the point group D<sub>3d</sub> to the irreducible representations of the group C<sub>2h</sub>. This leads to a reduction in degeneracy (E<sub>u</sub> → B<sub>u</sub> + A<sub>u</sub> and E<sub>g</sub> → B<sub>g</sub> + A<sub>g</sub>) with preservation of the alternative prohibition. Thus, for Si-O valency vibration bands should be observed in the absorption spectrum of thortveitite. Additional complication of the spectrum can be caused by resonance interaction between the ions in the crystal. The elementary cell of thortveitite (space group C<sub>2h</sub><sup>3</sup>) contains two Si<sub>2</sub>O<sub>7</sub> ions; Davydov's [7] theory suggests that there should be doublet splitting of all the internal vibrations of the ions, but the alternative prohibitions are not cancelled, and this is an approximation (Table 3). Of the four bands observed experimentally in the thortveitite spectrum, only one\* is a doublet, and this clearly corresponds to the vibration with the highest dipole moment. Thus, the results of ana-

\* That this frequency is somewhat higher than in the case of the other pyrosilicates may be explained by the shape of the Si<sub>2</sub>O<sub>7</sub> group, and by the greater interaction between Si-O and M-O bonds, probably partially due to a greater covalent character (with M = Sc, Er, Yb).

lysis of the infrared spectrum of thortveitite (and of the silicates of Er and Yb) are in full agreement with the data on its crystal structure.\*

It follows from the above that the rare earth element pyrosilicates can be divided into three groups, distinguished not only by their lattice structure, but also by the shape of the  $\text{Si}_2\text{O}_7$  group. We attempt below to discuss the role of various factors affecting the shape of the  $\text{Si}_2\text{O}_7$  group in the crystals investigated, although it is at present difficult to give a complete explanation of all the observed regularities. Following an idea of Belov's, that silicon-oxygen anions can "adapt themselves" to the dimensions of the cation, we can probably relate the change in shape of the  $\text{Si}_2\text{O}_7$  group and the crystalline structure of pyrosilicates to the "lanthanide contraction," i.e., to the decrease in ionic radius of the lanthanides with atomic number. This assumption also corresponds to a decrease in ionic radius in the series  $\text{La}^{+++} \rightarrow \text{Y}^{+++} \rightarrow \text{Sc}^{+++}$  [10]. On the other hand, the change in shape of the  $\text{Si}_2\text{O}_7$  group may also be interpreted as the result of a change in character of the bond  $\text{Si}-\text{O}$  and  $\text{Si}-\text{O}(\text{Si})$ , depending on the basicity of the cation. It is known that basicity diminishes up the series  $\text{La} \rightarrow \text{Lu}$ , Y is intermediate between Dy and Ho, and Sc follows after Lu [11]. We may suppose that, in the  $\text{Si}_2\text{O}_7$  ion bonded with cations by purely electrostatic interactions, the accumulation of electrons on  $\text{O}^-$  atoms makes possible some increase in the order of  $\text{Si}-\text{O}^-$  bonds, as the result of partial formation of  $p\pi-d\pi$  bonds. It follows that the  $\text{Si}-\text{O}-\text{Si}$  bonds approximate in character to simple p-bonds, and that the  $\text{SiOSi}$  angle tends to the value characteristic of such bonds ( $90^\circ$ ). With decreasing basicity of the cation, the increasing covalency of the  $\text{M}-\text{O}$  bonds leads to a reduction in order of the  $\text{Si}-\text{O}$  bonds, so that it becomes possible for the role of  $p\pi-d\pi$  interaction in the  $\text{Si}-\text{O}-\text{Si}$  bonds to increase, and therefore the  $\text{SiOSi}$  angle increases.

It also cannot be excluded that the existence of these three types of lanthanide pyrosilicate structures is not a matter of chance: The division of the cations into three groups possibly corresponds to the existence of the three most stable electronic configurations:  $\text{La}^{+++}$ ,  $\text{Gd}^{+++}$ , and  $\text{Lu}^{+++}$  (0, 7, and 14 electrons in the 4f shell). It may therefore be supposed that the difference in the electronic configurations of the cations of the three above-mentioned groups, and consequently the difference in the ionic fields created by these ions, determines the specific crystalline structure. However, this assumption is not in agreement with the inclusion of the Sc and Y silicate structures in the general scheme.

The authors would like to express their thanks to L. A. Bondar\*, F. Ya. Galakhov, and A. I. Leonov for providing the silicate samples, and to N. A. Toropov and E. F. Gross for their constant interest in this work.

#### SUMMARY

1. By an investigation of the infrared spectra of rare earth element silicates, it has been established that there are  $[\text{SiO}_4]^{4-}$  ions in compounds corresponding in composition to ortho- and oxyorthosilicates, and  $[\text{Si}_2\text{O}_7]^{6-}$  ions in compounds of pyrosilicate composition.

2. Depending on the nature of the cation, the rare earth element pyrosilicates give three types of crystalline structure with differently shaped  $\text{Si}_2\text{O}_7$  groups.

3. It is suggested that the difference in shape of the  $[\text{Si}_2\text{O}_7]^{6-}$  ions is associated with differences in the values of the ionic radii (and of the coordination polyhedra) of the cations, and with the associated changes in the nature of the bonds within the complex anions.

#### LITERATURE CITED

1. A. N. Lazarev, *Optika i spektr* **9**, 195 (1960).
2. A. N. Lazarev, *Kristallografiya* **6**, 125 (1961).
3. A. N. Lazarev and T. F. Tenisheva, *Optika i spektr* **10**, 79 (1961).
4. N. A. Toropov and I. A. Bondar\*, *Izv. AN SSSR, Otd. Khim. Nauk* **1959**, 554.
5. N. A. Toropov and F. Ya. Galakhov, *Izv. AN SSSR, Otd. Khim. Nauk* **1961**, 539.
6. R. S. Halford, *J. Chem. Phys.* **14**, 8 (1946).
7. A. S. Davydov, *The Theory of Light Absorption in Molecular Crystals* [in Russian] (Acad. Sci. Ukr.SSR, Kiev, 1951).

\* It has recently been suggested that there is some deviation from central symmetry in the structure of thortveitite [9]. However, our view is that the spectroscopic results indicate that such deviations are inconsiderable.

8. W. H. Zachariasen, *Z. Kristallogr.* **73**, 1 (1930).
9. G. A. Barclay and E. G. Cox, *Z. Kristallogr.* **113**, 23 (1960).
10. A. F. Wells, *The Structure of Inorganic Compounds* [Russian translation] (IL, Moscow, 1948).
11. D. Post, G. Ressel' and K. Garner, *Rare Earth Elements and Their Compounds* [Russian translation] (IL, Moscow, 1949).

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

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ADSORPTION OF VAPORS ON NONPOROUS SORBENT MODELS  
WITH A PHYSICALLY MODIFIED SURFACE  
COMMUNICATION I. LOW TEMPERATURE ADSORPTION OF NITROGEN  
ON CARBON BLACK WITH PREADSORBED WATER

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The idea of the physical modification of the surface of adsorbents has long attracted investigators working in the field of adsorption. However, the great experimental difficulties involved in preparing the modified surface has led to the fact that at the present time only a small number of papers on this subject are to be cited in literature which are far from embracing all the possibilities offered by this method, [1-5].

Physical modification of the adsorbent surface may be accomplished through preliminary adsorption of the vapor of some relatively high boiling substance or modifier with subsequent quick lowering of the adsorbent temperature down to a vanishingly small modifier vapor pressure over the adsorbent. As a result, the adsorbed film which corresponds with the conditions under which the adsorption of the modifier vapor took place is, as it were, "hardened" and the way in which the adsorbent surface was filled up is made permanent. One can study the low temperature adsorption of the vapor of another substance on a modified adsorbent of this sort.

The purpose of the investigation presented in this series of papers is an attempt to use the method of physical modification of the adsorbents to study the nature of surface filling by preadsorbed substances and to study the adsorptional properties of the modified surfaces. In the present first communication of this series, we give the results of experiments on the effect which physical modification of a carbon black surface by water has on the low temperature adsorption of nitrogen.

#### EXPERIMENTAL

As the adsorbant we used thermal black baked in vacuum at 950°, with a specific surface  $\sim 32 \text{ m}^2/\text{g}$ . This choice was dictated on the one hand by the fact that we wanted to reduce the porosity effect, which makes the results difficult to interpret, and on the other hand, by the fact that we wanted to have a surface with a chemical nature as close as possible to the surface of active charcoals. With the thought in mind that subsequently these data could be applied to active charcoals. The adsorbate was nitrogen at its boiling point and as the preadsorbed substance water was used. The nitrogen was prepared by thermal decomposition in vacuum of chemically pure sodium azide. The distilled water was degassed in vacuum.

The investigation was carried out gravimetrically on a setup using the high-sensitivity adsorption balance described previously in [6], since this method allows direct measurement of the quantitative preadsorbed substance after it has been frozen. Actually the balance has been subjected to some slight changes which improve its stability. In particular, to reduce the effective convection currents which inevitably arise when large temperature differences are present, the balance was made asymmetric as possible. In this way we were practically able to eliminate the effect of convection currents on the balance readings completely. The sensitivity of the balance was  $2.08 \cdot 10^{-7} \text{ g}$ . A 59 mg sample of carbon black pressed without binder into a tablet  $\sim 4 \text{ mm}$  in diameter, was placed in a platinum cup suspended on one end of the beam of the balance. On the other end of the beam was suspended a platinum counterweight, balancing the initial weight of the carbon black in the cup. Before every series of experiments the carbon black sample was heated on the balance in vacuum at 400° to constant weight. A nitrogen gas thermometer was used to measure the temperature of the liquid nitrogen.

First, the adsorption isotherm of nitrogen on pure carbon black at  $-195^\circ$  was taken (curve 1, Fig. 1). Then after pumping off and heating the carbon black, a fixed quantity of water vapor was absorbed on it at  $20^\circ$ , and helium was admitted to the apparatus at a pressure of 20-50 mm Hg. After this, the sample was quickly cooled to liquid nitrogen temperature and pumped off. The helium was admitted to the apparatus to improve the heat conduction between the walls of the balance housing and the adsorbent suspended on the balance and at the same time to reduce the mass exchange between the adsorbent and the colder walls of the balance housing during cooling, [3] and [5]. This precaution allowed us to cool the adsorbent to  $-195^\circ$  without any substantial loss of adsorbed water. The quantity of pre-adsorbed water was measured directly from the increase in weight. Then came the usual nitrogen adsorption measurements, the adsorbent was again pumped off, another layer of water was adsorbed, etc.

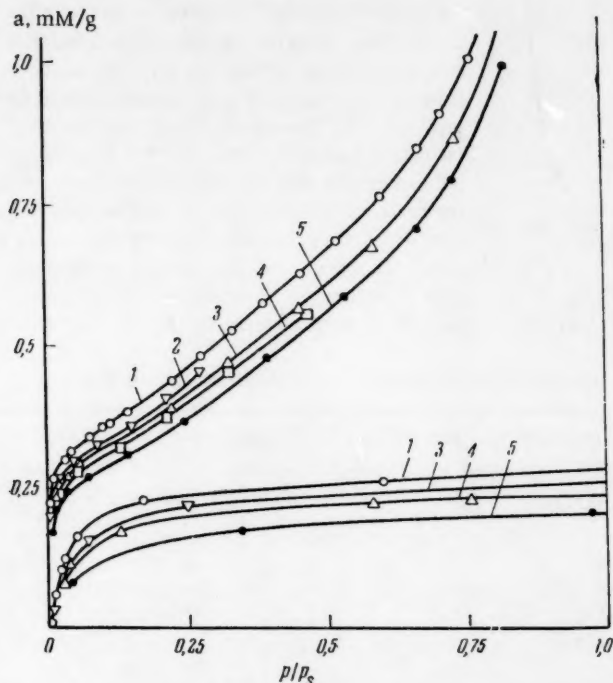


Fig. 1. Nitrogen adsorption isotherms at  $-195^\circ$  on pure carbon black, curve 1, and on carbon black with increasing quantities of preadsorbed water, curves 2, 3, 4, and 5. The lower curves are the initial portion of the upper curves with the scale of  $p/p_s$  increased 100 times.

In this way we obtained the adsorption isotherms of nitrogen on carbon black with different amounts of pre-adsorbed water (curves 2-5, Fig. 1). Using the adsorption isotherm of water vapor on the same carbon black taken on the usual vacuum sorption balance at  $20^\circ$ , we determined what points on the isotherm the measured quantities of preadsorbed water corresponded with and thus calculated the degree of completion of the monomolecular layer  $\theta$  which they represent (Table 1). The value of  $\theta$  was calculated from the known surface of the carbon black in the area occupied by a molecule of water on the carbon black surface,  $\omega = 14.8 \text{ \AA}^2$  [7]. As may be seen from Table 1, the maximum amount of preadsorbed water was 2.5 layers. We were not able to get any more on, since at relative pressures  $p/p > 0.966$  the amount of water vapor adsorbed on the carbon black is very strongly dependent on the pressure (Fig. 2). Therefore, even an insignificant drop in the water vapor pressure during freezing could cause substantial desorption in spite of the rapid cooling in the presence of the helium.

The nitrogen adsorption isotherms on pure carbon black and on carbon black with preadsorbed water have a form corresponding to the type II isotherms of Braunauer's Classification. It is a matter of fundamental importance that the nitrogen adsorption at different relative pressures decreases systematically with increase in the amount of preadsorbed water (compare curves 1-5, Fig. 1), the reduction being nearly proportional to the amount of preadsorbed water.

The BET equation gives a good description of the experimental data in the relative pressure range  $p/p_s = 0.05-0.4$ . However, the experimental points in the linear form of the B.E.T. equation representing  $h/a (-h) = f(h)$ , where  $h = p/p_s$  formed two sharply defined linear segments with different slopes: one in the range of  $p/p_s$  from 0.003 to 0.15 and the other from 0.15 to 0.4. The constants of the equation calculated from the straight line drawn through the

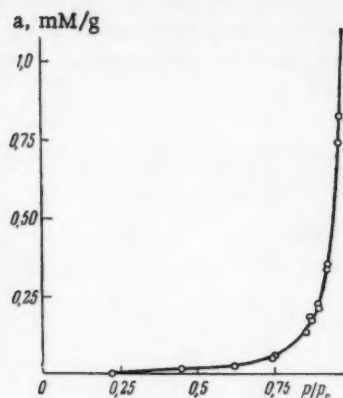


Fig. 2. Adsorption of isotherm of water vapor on carbon black at 20°.

experimental points in the first segment are substantially different from the constants calculated from the second segment or from an averaged straight line embracing the whole  $p/p_s$  region from 0.003 to 0.4. There is a particularly large difference in the constant  $c$ , which in the first segment is equal to about 300, and in the second segment is reduced to 60-40. Following the advice of MacIver and Emmett, [8], the constants we used in calculation were taken from the first linear segment of the B.E.T. equation, since the constant  $a_m$ , equal to the amount of adsorption with a completed monomolecular layer, lies in precisely this relative pressure region. For all the isotherms the quantity  $a_m$  is approximately the one for the relative pressure  $p/p_s = 0.065$ . The results of applying the B.E.T. equation to the experimental data are given in Table 1. The specific surfaces were calculated under the assumption that the nitrogen molecule occupies an area of  $16.2 \text{ \AA}^2$  on the carbon black surface. As may be seen from Table 1, the specific surface decreases systematically with increase in the amount of preadsorbed water. In spite of the fluctuations in the value of  $c$  because of the low degree of accuracy with which it can be determined ( $\sim \pm 10\%$ ), the tendency for it to be reduced from 300 to 200 may be easily observed.

TABLE 1. Nitrogen Adsorption at  $-195^\circ$  on Modified Carbon Black

Isotherm number	Preadsorbed water vapor			Nitrogen adsorption at $-195^\circ$			
	a, mM/g	$p/p_s$	$\theta$	a, mM/g	$c$	$S, \text{m}^2/\text{g}$	Range of applicability $p/p_s$
1	0	—	—	0,332	300	32,4	0,005—0,15
2	0,354	0,920	1,0	0,312	290	30,4	0,003—0,15
3	0,495	0,936	1,4	0,298	300	29,1	0,003—0,18
4	0,795	0,962	2,2	0,288	270	28,1	0,003—0,15
5	0,901	0,966	2,5	0,270	200	26,4	0,003—0,18

To find the causes of the reduction in the specific surface of the adsorbant, the reduction in the constant  $c$  and the amount of nitrogen adsorbed, as the quantity of preadsorbed water is increased we found the nitrogen adsorption isotherm on frozen water at  $-195^\circ$ . For this purpose, we used the usual volumetric apparatus. Highly dispersed ice was prepared by freezing water vapor directly on the walls of a glass ampule 20 mm in diameter and 60 mm long. Here the first ampule had a second ampule full of water sealed onto it. The water was degassed in vacuum by pumping out about 1/5 of the volume. Then the first ampule was immersed in the cooling mixture, and the water from the second ampule was frozen over onto the walls of the first ampule. After the necessary quantity of water had been frozen over, the second ampule was shut off from the first by a stop cock. The dead volume in the ampule was measured with helium. A nitrogen gas thermometer was used to measure the temperature of the liquid nitrogen.

Since ice has several crystalline forms existing at different temperatures, we made several series of measurements of the nitrogen adsorption isotherms on ice under different conditions of cooling down to the temperature of liquid nitrogen, and with different amounts of water frozen over from 0.5 to 15 g. As a result, it became clear that ice prepared at the temperature  $-(50-70^\circ)$  and then quickly cooled to  $-195^\circ$  forms a total surface of several square meters. The accuracy of the adsorption measurements in such cases was very small. However, if the ice collected on the walls of the ampule is immediately cooled down to  $-195^\circ$  it has a total surface of 110-150  $\text{m}^2$ , and this surface value is only slightly dependent on the quantity of water frozen over. Obviously, the adsorbing surface is formed only on a thin surface layer of ice. As the quantity of water frozen over is increased, the lower lying ice crystals probably continue to grow until they are completely interlocked with one another. This may be confirmed visually,



since if large quantities of water are frozen over, the layers adhering to the walls of the ampule look solid and almost transparent, while the layers formed in the interior of the ampule were loose and white.

The isotherms obtained were described by the B.E.T. equation which made it possible to calculate the specific surfaces, assuming that the nitrogen molecule occupies an area of  $16.2 \text{ \AA}^2$  on the ice. The isotherms measured each time on a new part of the ice are all in good mutual agreement on a graph plotted to the coordinates; adsorption, referred to unit surface, against relative pressure. Curve 6 of Fig. 3 gives the experimental points from three independent series of measurements of the adsorption of nitrogen on ice crystals at  $-195^\circ$ . In the same Fig. 3, curve 1 gives the adsorption isotherm of nitrogen on pure carbon black. As may be seen from the graph, the rate of rise of the adsorption isotherms of nitrogen on ice is, in the initial region, considerably less than the rate of rise of the isotherm on carbon black. Correspondingly, for the isotherm 6, the constant  $c$  is about equal to 60.

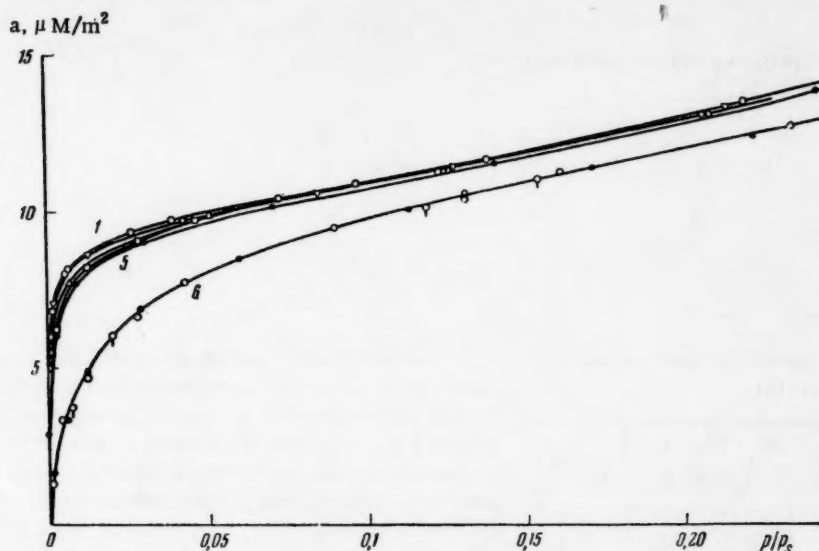


Fig. 3. Nitrogen adsorption isotherms at  $-195^\circ$  on pure carbon black, curve 1, carbon black with preadsorbed water, curves 2-5, and on ice crystals, curve 6 (three series of measurements).

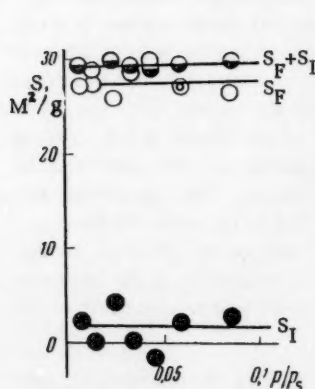


Fig. 4. Surfaces of carbon black and ice calculated additively.

Comparison of the isotherms 2-5 with the isotherms 1 and 6, showed that strictly speaking, they are not additive but isotherms 2-5 are considerably closer in form to isotherm 1 and to isotherm 6. Consequently, the adsorption of nitrogen on carbon black with preadsorbed water is by nature closer to the adsorption on pure carbon black than on ice, even with such large quantities of preadsorbed water that if the carbon black particles are covered uniformly, about two or three adsorbed layers could be formed.

#### Discussion of Experimental Results

The reasons for the fact that preadsorbed water has so little effect on the adsorption of nitrogen on pure and modified carbon black are probably the following: (a) the ice formed from preadsorbed water is fundamentally different from the ice prepared by freezing water vapor directly onto the walls of the glass ampule; (b) the adsorbed water molecules even when they are two or three monomolecular layers thick do not really shield the adsorption field of the carbon black and so have little effect on the nitrogen adsorption; (c) an adsorbed water layer one to three molecules thick acting under the surface field of the adsorbant forms a field of adsorption forces over top of itself which is very similar to the carbon black field; (d) the water adsorbed on the carbon black does not form continuous adsorbed layers but collects into islets which cover only a small part of the carbon black surface. The last explanation given seems to us to be the most probable one since

it is in agreement with the ideas which have been developed in our laboratory on the subject of water vapor adsorption on carbonaceous adsorbents [9 - 13].

Following the islet scheme the preadsorbed water covers only part of the carbon black surface, namely the surface  $S_I$ , leaving the part  $S_F$  of the carbon black surface free. Let us now try to calculate these surfaces. From the isotherms 1 and 6 of Fig. 3, we can find the amount of nitrogen adsorbed per unit surface for pure carbon black,  $a_F$  and for ice,  $a_I$ . In addition, we know the total adsorption of nitrogen on carbon black with preadsorbed water,  $a_{FI}$ , from curves 2-5 of Fig. 1. Obviously, for a given relative pressure we are justified in writing the following equation:

$$S_I a_I' + S_F a_F' = a_{FI}' \quad (1)$$

and in the same way, for another relative pressure

$$S_I a_I'' + S_F a_F'' = a_{FI}'' \quad (2)$$

Solving these equations simultaneously we obtain

$$S_I = \frac{a_{FI}' a_F'' - a_{FI}'' a_F'}{a_F' a_I'' - a_F'' a_I'} \quad (3)$$

and

$$S_F = \frac{a_{FI}' a_I'' - a_{FI}'' a_I'}{a_F' a_I'' - a_F'' a_I'} \quad (4)$$

TABLE 2. Results of Calculations from Equations (3) and (4)

Isotherm number	$S_F$ m <sup>2</sup> /g	$S_I$ m <sup>2</sup> /g	$S_F + S_I$ m <sup>2</sup> /g	$S$ from BET
2	29,2	1,1	30,3	30,4
3	27,4	1,8	29,2	29,1
4	23,8	4,5	28,3	28,1
5	22,3	4,1	26,4	26,4

We have carried out this calculation for a range of relative pressures from 0.005 to 0.1. As an example, Fig. 4 shows the results of the calculations for isotherm 3. It must be kept in mind how small the accuracy of calculation of  $S_F$  and  $S_I$  is, since from Eq. 3 and 4, they are obtained as the quotient of differences of very nearly equal quantities, taken directly from graphs, and the maximum absolute error, calculated from the theory of errors, may reach  $\pm 5$  m<sup>2</sup>/g. Nevertheless, the maximum spread of the points for  $S_I$  and  $S_F$  does not exceed  $\pm 3.5$  and  $\pm 2.8$  m<sup>2</sup>/g respectively, which justifies finding mean values for these quantities which are given as solid lines on the graph. The mean values resulting from the calculations are given in Table 2.

Some measure of the correctness of the calculation is given by the good agreement between the total surface  $S_F + S_I$  and the specific surface determined from the B.E.T. equation. The calculations show that the ice surface is small compared with the free carbon black surface, and a continuous lamina coating on the carbon black formed from adsorbed and frozen water does not occur. Here the total surface  $S_F + S_I$  drops off systematically. To test this conclusion we made a calculation for an imaginary adsorbent consisting of a mixture of pure carbon black and ice crystals taking 95, 90 and 80% of the surface as carbon black and 5, 10 and 20% respectively of the surface as ice. Taking the same fractions of the adsorptions  $a_F$  and  $a_I$  from isotherms 1 and 6 of Fig. 3, and taking the total surface to be 32.4 m<sup>2</sup>/g, we treated these artificially constructed isotherms according to the B.E.T. system. The calculations showed that the specific surface remains constant, and within the limits of error is equal to 32.4 m<sup>2</sup>/g, while the constant  $c$  drops off systematically. In addition, all the isotherms if they were drawn in Fig. 1 (they are not given on the graph) would go between curves 1 and 2, practically coinciding with Fig. 1 at  $p/p_s > 0.1$ . Consequently, if the isotherms for these imaginary adsorbents are going to fit the isotherms 2-5 completely, it is necessary to take account of the reduction in their specific surface.

Using the specific surfaces  $S_F + S_I$  which we have found, we can calculate the amount of adsorption per unit adsorbent surface and plot the isotherms 2, 3, 4, and 5 in Fig. 3. As may be seen from Fig. 3, these isotherms almost correspond with curve 1, Fig. 1, and are far away from curve 6. This last fact also causes us to think that modifying a carbon black surface with water causes a reduction of the original surface, thus causing the nitrogen adsorption to drop off as the quantity of preadsorbed water is increased.

We shall now consider in just what way the reduction in the total surface can occur. Let us return again to the assumption that the water covers the carbon black in a uniform adsorbed layer, and let us see how the total adsorbent surface will change in an adsorption scheme of this sort. Electron microscope photographs show that the carbon black consists of particles having a regular spherical form (Fig. 5), the diameter of which varies from 0.3 to 0.015  $\mu$ . A statistical analysis of these photographs shows that the mean diameter of the particles is  $\bar{d} \approx 0.1 \mu$ . On the other hand, using the known surface value for carbon black of  $S = 32.4 \text{ m}^2/\text{g}$ , found from the B.E.T. equation, and taking the density of carbon black to be  $\delta = 1.80 \text{ g/cm}^3$ , we calculated the diameter of the particles, considering them to be dispersed in a monolayer. The result was  $\bar{d} \approx 0.1 \mu$  and the number of particles per gram of carbon black was found to be  $n_F \approx 1 \cdot 10^{15}$  per gram. The good agreement between the two values of  $\bar{d}$ , calculated by two different methods is apparently fortuitous, but all the same it supports the fact that we are dealing with a nonporous adsorbent, the geometric surface of which is very nearly the same as the surface on which the nitrogen adsorption is taking place. Taking the thickness of the adsorbed film of water to 2 Å, it may easily be shown that with two points of contact for each particle, the total surface will be increased by the adsorbed film to  $32.7 \text{ m}^2/\text{g}$ , and that it is only with six points of contact that it will become equal to  $32.4 \text{ m}^2/\text{g}$ , which is the original surface of the carbon black. Thus, it becomes clear that a uniform coating of water on the carbon black will not explain the overall reduction in surface.

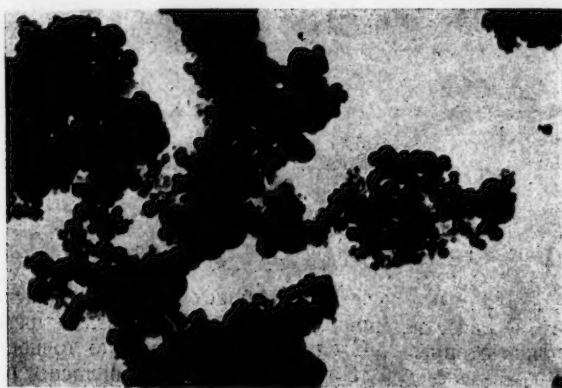


Fig. 5. Electron microscope photograph of carbon black (magnification  $\times 29,000$ ).

If we assume that the water, adsorbed in the form of separate islets, has been frozen and converted into separate crystals or groups of crystals on the carbon black surface, it may easily be shown, that in this case any amount of reduction in the carbon black surface may occur, but the surface of the ice crystals deducting the surface which they have in common with the carbon black, will always be greater than the surface which they occupied on the carbon black surface, and, consequently, the total surface will become greater than the original surface, which is in contradiction both with the data calculated from the B.E.T. equation and from our own calculations. Thus, this scheme for the adsorption of water vapor on the carbon black surface drops out of the picture.

We shall assume further that a considerable quantity of the preadsorbed water is located at the points of contact between the carbon black particles, leaving the rest of the surface essentially free. If we want to verify this last assumption, we can look at the papers by Radushkevich [14 - 18], who has solved the problem of capillary condensation in highly dispersed systems. Unfortunately, we cannot use the exact solution for a poly-dispersed system of contacting particles, since we do not know how the number of contacts between particles of different radii is distributed. However, as a qualitative estimate, we can consider our system to be mono-dispersed, taking an arbitrary coordination number, i.e., the number of contacts  $\mu$  which one particle makes with the other is taken to be three or four, which is the most probable value for a system of this sort.

According to Radushkevich [4], the volume of water condensed in the space between two contacting particles is given by the equation

$$V' = \frac{2}{3} \pi r^3 U, \quad (5)$$

where  $\underline{r}$  is the radius of the particles;  $U = f(\beta)$ , and  $\underline{b} = c/r$ , where in turn

$$c = \frac{2\sigma v}{RT \ln p_s/p} \quad (6)$$

$\sigma$  is the surface tension;  $v$  is the molar volume of the adsorbate, and  $R$  is the gas constant. Taking in our case  $\sigma = 72.8$  dynes/cm,  $v = 18$  cm<sup>3</sup>/M,  $R = 8,315 \cdot 10^7$  erg/deg·M and finding  $p/p_s$  from Table 1, we made the necessary calculations. The results are given in Table 3. The 6th and 7th columns of the table give the volumes of water condensed in the spaces between the carbon black particles calculated by Radushkevich's method for 3 and 4 points of contact, and the last column gives the actual amount of preadsorbed and frozen water. As can be seen, these values are very close to one another. This gives reason to suppose that in accordance with the scheme, some rather large part of the preadsorbed water is located at the points of contact between particles.

Further, following Radushkevich, we shall calculate the decrease in carbon black surface caused by the condensation of water vapor in the spaces between the contacting particles [18]. The decrease in surface is given by the equation

$$\Delta S = S_0 v s', \quad (7)$$

where  $s' = f(\beta)$  and  $S_0$  is the original surface. The results of these calculations together with the surfaces calculated previously on an additive basis are given in Table 4.

TABLE 3. Amounts of Water Condensed in the Spaces between Contacting Particles (after Radushkevich)

Isotherm number	$p/p_s$	$\beta$	$U \cdot 10^4$	$V', \text{cm}^3 \cdot 10^{18}$	$V \text{ at } \nu=3, \text{mm}^3/\text{g}$	$V \text{ at } \nu=4, \text{mm}^3/\text{g}$	$V \text{ exper. mm}^3/\text{g}$
1	2	3	4	5	6	7	8
2	0,920	0,125	4,9	1,45	4,31	5,75	6,37
3	0,936	0,162	7,5	2,22	6,30	8,80	8,92
4	0,962	0,267	14,3	4,24	12,6	16,7	14,3
5	0,966	0,293	17,3	5,12	15,2	20,3	16,2

TABLE 4. Change in Carbon Black Surface from Water Condensed in the Spaces Between Contacting Carbon Black Particles (after Radushkevich)

Isotherm number	$s'$ fract.	$S_{\nu=3}, \text{m}^2/\text{g}$	$S_{\nu=4}, \text{m}^2/\text{g}$	$S_F, \text{m}^2/\text{g}$
2	0,0244	30,0	29,2	29,2
3	0,0305	29,4	28,4	27,4
4	0,0458	28,0	26,5	23,8
5	0,0493	27,6	26,0	22,3

It follows from Table 4 that the decrease in surface caused by the condensation of adsorbed water in the spaces between the contacting particles is perfectly capable of reaching the same kind of values which can be found in the calculations given above.

Thus, the scheme explains the reduction in adsorptional surface as the quantity of preadsorbed water is increased, however, it requires complete wetting of the carbon black surface by water so that condensation can occur between the contacting particles, which contradicts our own premise, that the carbon black is not completely covered by an adsorbing water film.

We shall now envisage another method of explaining the phenomenon observed. So far we have considered the carbon black particles to be smooth. Now, we shall assume that the carbon black surface exhibits micro-roughness, which consists of small depressions. If the surface of the carbon black particles consists essentially of the basal planes of carbon crystals, the surface of the depressions will be formed by the lateral surfaces of the crystals, which contain carbon atoms having unsaturated valences, which are able to bind oxygen atoms, i.e., to form surface oxides or primordial adsorption centers. In this case, the water molecules will be adsorbed principally on the internal surface of the depressions and will there form the water islets which, on coalescing, fill up the depressions, i.e., they flatten out the overall surface or at any rate, the surface which is responsible for the adsorption of nitrogen molecules.

Now let us see how realistic this scheme is. Let us assume that the depressions on the carbon black surface are hemispherical in form and have radius  $\underline{r}$ . In this case, the total surface,  $S_1$ , of pure carbon black will consist of a "flat surface"  $S_{\text{—}}$  and the internal surface of the depressions,  $S_d$ . If the number of depressions in one gram of carbon black is  $n_d$ , then



$$S_1 = S_- + S_D = S_1 + n_D \frac{4\pi r^2}{2}. \quad (8)$$

However, if all the depressions are filled with water to the point where they are level with the "flat surface," the surface of the modified carbon black,  $S_M$ , will consist of the same "flat surface"  $S_-$  and the spherical areas of radius  $r$  belonging to the surface of the water which fills up the depressions, thus:

$$S_M = S_- + n_D \pi r^2 \quad (9)$$

Knowing  $S_1$  for the original carbon black and taking the value of  $S_M$  from the B.E.T. equation calculated for anyone of the isotherms 2-5, we can calculate  $n_D \pi r^2$ , i.e., the ice surface which is accessible for the adsorption of nitrogen molecules. The values found are very close to the values of  $S_1$  calculated additively. For example, for isotherm 5,  $n_D \pi r^2 = 6.0 \text{ m}^2/\text{g}$ , and  $S_1 = 4.1 \text{ m}^2/\text{g}$ . The values of  $n_D$  and  $r$  may be calculated in the following way. Let us assume that all the preadsorbed water is located in the depressions and fills them completely, giving

$$V_{\text{Exp.}} = n_D \cdot \frac{1}{2} \cdot \frac{4}{3} \cdot \pi r^3. \quad (10)$$

Knowing the value of  $n_D \pi r^2$  we find  $n_D$  and  $r$  from Eq. (10). The isotherm 5 gives  $r \approx 40 \text{ \AA}$  and  $n_D \approx 1 \cdot 10^{17}$ , i.e.,  $\sim 100$  depressions on one particle, which in order of magnitude is quite probable, since the roughness coefficient of carbon black obtained in this way is  $\alpha = 1.23$ . The micro-roughness scheme here considered turned out to be too much simplified. However, in spite of its poor quantitative agreement with experimental data, it gives a qualitative explanation of the nature of the changes observed in the specific surfaces.

Probably, the adsorption of water on a carbon black surface is a more complicated process, involving filling of the micro-roughness of the carbon black surface, condensation between contacting particles, adsorption on the "flat surface" and possibly even some redistribution of the water molecules on cooling. In subsequent communications, we shall return to a more detailed discussion of the schemes presented, supported by additional experimental material.

In conclusion, the authors recognize their pleasant obligation to express thanks to B. P. Bering, V. V. Serpinskiĭ, and L. V. Radushkevich for valuable advice and discussion of the results of the investigation.

#### SUMMARY

1. The change in adsorption of nitrogen on a carbon black surface at  $-195^\circ$  has been studied as a function of the quantity of preadsorbed water vapor.

2. Analysis of the experimental data leads to the preliminary conclusion that the preadsorbed water does not form continuous adsorbed layers on the carbon black surface.

#### LITERATURE CITED

1. P. H. Emmett, Chem. Revs. 1948, 43, 1, 69.
2. M. M. Dubinin and E. D. Zaverina, *Za. fiz. khimii* 23, 57 (1949).
3. I. H. Singleton and G. D. Halsey, Jr., J. Phys. Chem. 58, 330 (1954).
4. R. M. Barrer and L. V. Rees, Trans. Faraday Soc. 50, 852 (1954).
5. B. P. Bering, M. M. Dubinin, E. G. Zhukovskaya, and V. V. Serpinskiĭ, Doklady Akad. Nauk SSSR 130, No. 4, 793 (1960).
6. B. P. Bering and V. V. Serpinskiĭ, Doklady Akad. Nauk SSSR 94, No. 3, 497 (1954).
7. W. D. Harkins and G. Iura, J. Amer. Chem. Soc. 66, 1366 (1944).
8. D. S. MacIver and P. H. Emmett, J. Phys. Chem. 60, 824 (1956).
9. M. M. Dubinin and E. D. Zaverina, *Zh. fiz. khimii* 21, No. 12, 1373 (1947).
10. N. N. Avgul', O. M. Dzhigit, and A. V. Kiselev, Doklady Akad. Nauk SSSR 86, No. 1, 95 (1952).
11. B. P. Bering and V. V. Serpinskiĭ, Izv. AN SSSR Otd. Khim. Nauk 1953, 957.
12. M. M. Dubinin and E. D. Zaverina, Izv. AN SSSR Otd. Khim. Nauk 1954, 217.
13. N. N. Avgul', O. M. Dzhigit, A. V. Kiselev, and K. D. Shcherbakova, Doklady Akad. Nauk SSSR 92, No. 1, 105 (1953).
14. L. V. Radushkevich, Izv. AN SSSR, Otd. Khim. Nauk 1958, 1008.



15. L. V. Radushkevich, *Izv. AN SSSR, Otd. Khim. Nauk* 1958, 285.
16. L. V. Radushkevich, *Izv. AN SSSR, Otd. Khim. Nauk* 1958, 403.
17. L. V. Radushkevich, *Izv. AN SSSR, Otd. Khim. Nauk* 1960, 756.
18. L. V. Radushkevich, *Izv. AN SSSR, Otd. Khim. Nauk* 1960, 984.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

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# INVESTIGATION OF CAPILLARY CONDENSATION OF VAPORS IN HIGHLY DISPERSED SYSTEMS

## COMMUNICATION 5. ANALYSIS OF THE JOINT PROCESS OF ADSORPTION AND CAPILLARY CONDENSATION IN SYSTEMS OF CONTACTING PARTICLES

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In a previous work [1] we have discussed the process of capillary condensation of vapors in a system of a large number of particles which are in contact with one another. The results obtained from this calculation, however, can be compared with experimental data only if the adsorption of vapor on the surface of (nonporous) contacting particles is taken into consideration as well as the capillary condensation, since the magnitude of the adsorption in the general case cannot, obviously, be ignored. Experimentally obtained sorption isotherms in some degree characterize superposition of the two sorption processes.

In work by other authors [2] devoted to the sorption processes in systems of contacting particles, an analysis is given of the joint process of adsorption and capillary condensation, but the characteristics of the structure of these systems are expressed schematically and conditionally. Yet for even the simplest case of nonporous particles the real structural characteristics of the system may prove to be determining factors both for adsorption and for capillary condensation. An investigation carried out by us [1] showed that three types of statistical distribution are characteristic of such systems: a) with respect to the size of the particles; b) with respect to the number of contacts per particle; c) with respect to the magnitude of the irregularities on the surface of the particles; the last two distributions depend on the first. Thus, the problem can be resolved in a well defined way if the distributions mentioned are known. But, since the information on them is still insufficient, we are not in a position to analyze quantitatively the whole process of sorption. This forces us to limit our description to a qualitative basis.

The total magnitude of the sorption  $\underline{a}$  per unit of mass of the system is the sum of the adsorption  $a_a$  and the capillary condensation  $a_k$ , i.e.,

$$a = a_a + a_k \quad (1)$$

Obviously,  $\underline{a}$  is a function of the relative vapor tension  $p/p_s$ , since both of the contributing items depend on the magnitude of the latter. It is entirely permissible to assume that with rather small values of  $p/p_s$  capillary condensation is absent and consequently the second item in (1) becomes zero, i.e., under these conditions the process lies in the realm of pure adsorption. At elevated pressures both items may be commensurate. Finally, at large values of  $p/p_s$  the magnitude of  $a_a$  may become considerably less than that of  $a_k$ , for example, for smooth spheres tightly packed or for flattened particles which touch one another in areas of ultimate size.

With an increase in the size of the particles both values  $a_a$  and  $a_k$  decrease, as can be seen from our calculations in the first communication [3] and will here be further shown. Thus highly dispersed systems on the whole have a greater sorption capacity per unit of mass.

A change in the number of contacts occurs in going from loose systems to closely packed ones, obtained for example, by compression.

### Adsorption of Vapor in a System of Contiguous Particles

Although in the case of nonporous particles adsorption takes place on their outer surface, for a description of this process in the general aspect it is insufficient to just know the adsorption isotherm obtained for an indefinitely large

adsorbing surface, since the process in a given system is complicated by at least two causes: 1) starting at some relative vapor pressure, with capillary condensation, part of the surface will be occupied by liquid sorbate and adsorption will proceed only on the remaining free surface of the particles, while the latter will continuously decrease with an increase in  $p/p_s$ , which should be taken into account in describing the adsorption; 2) between the adsorption film and the edge of the meniscus of the liquid close to points of contact of the particles there is a transitional region of filling where the process cannot be described either by means of the theory of capillary condensation or by means only of polymolecular adsorption. Attempts to analyze this transitional region have not yet led to a final solution of this problem [4]. The main volume of the capillary-condensed material, however, is in direct proximity to the contact point, while the main mass of the purely adsorbed material lies at points removed from contact. Therefore in an evaluation of the total magnitude of sorption it seems possible to ignore the transitional region and to assume the summation of the two components of the sorption process. Thus, the first of the complications mentioned should be considered primarily. We shall limit ourselves here to systems of contacting particles of the same size with free packing.

When two ideal identical spherical particles are in contact with each other, the surface of each of them which is lost for adsorption is a side surface of a spherical segment of height  $z_0$ , corresponding to the boundary position of the meniscus of the liquid at the point of contact. For a particle of radius  $R$  this surface is

$$S_1 = 2\pi R z_0.$$

From simple geometric constructions it follows that

$$z_0 = R \left( 1 - \sqrt{1 - x_0^2} \right),$$

if  $x_0 = r_0/R$ , where  $r_0$  is the radius of the circumference of a principal spherical segment. For a given  $R$  the boundary position of the meniscus is characterized by a point of contact of the arc of a trochoid (or at  $p/p_s = 1$ , that of an arc of a catenary) and a circle of radius  $R$ . Consequently  $x_0$  can be determined for various values of  $\beta = C/R$  or of  $p/p_s$  from data from the solution of the general problem of the capillary condensation between two spherical particles. The magnitude of  $x_0$  has been calculated by us previously [3] for different values of  $\beta$ . These results are given in the table. Hence the surface occupied by the meniscus on one sphere is

$$S_1 = 2\pi R^2 \left( 1 - \sqrt{1 - x_0^2} \right).$$

The fraction of the surface of the sphere occupied by the meniscus is

$$s = 1/2 \left( 1 - \sqrt{1 - x_0^2} \right)$$

The values of  $s$  are given in the table. If a sphere is in contact on the average with  $\nu$  spheres, then the fraction of its surface lost for adsorption is  $\nu s$ , and the average free surface of a sphere on which the process of adsorption occurs is

$$S_2 = S - \nu S_1 = 4\pi R^2 (1 - \nu s)$$

Let the magnitude of the adsorption of a given vapor on a nonporous adsorbent be  $a_1$  mm/cm<sup>2</sup>, while  $a_1 = f(p/p_s)$ . Then obviously the magnitude of the adsorption on 1 g of packed spheres touching one another, taking into account the capillary condensation, is

$$a_a = \frac{3a_1}{\rho_p R} (1 - \nu s) = a_0 (1 - \nu s), \quad (2)$$

where  $\rho_p$  is the density of the nonporous particles, and  $a_0$  is the magnitude of the adsorption in millimoles up to the beginning of capillary condensation, when  $s = 0$ , i.e.,  $a_0 = 3a_1/\rho_p R$ . From the preceding it follows that the average  $s$  is a function of  $p/p_s$ , therefore

$$a_a = f(p/p_s) [1 - \nu \cdot \theta(p/p_s)]. \quad (3)$$

This expression is the equation of the adsorption isotherm for a system of contacting spheres.

It is not difficult to pass to rough particles or to particles of irregular shape. If the weight radius of such particles is  $A$  and the radius of curvature of the same surfaces is  $R$ , then the meniscus-free surface of the particles is

$$S_2 = 4\pi A^2 (1 - \chi^2 \nu s),$$

$\chi = R/A$  and  $s$  has the previous significance;  $\nu$  is the number of contacts on the average on one particle.

The equation of the adsorption isotherm for rough particles, in conformance with the previously written relationship, takes the form

$$a_a = F(p/p_s) [1 - \chi^2 \nu \cdot \theta(p/p_s)]. \quad (4)$$

Application of formulas (3) and (4) is possible in those cases where the equations of the adsorption isotherm are known for the given structure of the surface of the adsorbent, i.e., where  $f(p/p_s)$  and  $F(p/p_s)$  are given. The function  $s = \theta(p/p_s)$  in any case can be found easily, since from the table it is possible to find the values of  $s$  at different values of  $\beta$ , right up to  $\beta = \infty$  at complete wetting.

$\beta$	$x_0$	$s$	$\beta$	$x_0$	$s$
0,05	0,212	0,0114	0,60	0,548	0,0817
0,10	0,282	0,0203	0,80	0,588	0,0957
0,20	0,377	0,0369	1,00	0,614	0,1053
0,30	0,437	0,0502	1,50	0,652	0,1209
0,40	0,482	0,0618	$\infty$	0,825	0,2174
0,50	0,518	0,0723			

Total analysis of the two formulas (3) and (4) shows that the magnitude of the adsorption decreases with an increase in the number of contacts occurring on the average on one particle, and also decreases when there is an increase in the area  $s$  occupied by the meniscus, which in turn increases with the relative vapor tension  $p/p_s$ , as follows from the table. Furthermore, from (4) it is seen that for rough particles the decrease in  $a_a$  is less than for smooth particles, since  $\chi$  is less than unity.

#### Joint Course of Adsorption and Capillary Condensation Processes in Various Systems of Contacting Particles

In considering the joint course of the adsorption process and capillary condensation in the systems under discussion it is necessary to give attention to several factors which variously influence the total magnitude of sorption in different regions of relative pressure  $p/p_s$ . In the simplest case of an uncomplicated process, where there are only separate menisci in the system, the magnitude of  $a_k$  increases in proportion to the average number of contacts  $\nu$ , while  $a_a$  decreases linearly with the increase in  $\nu$ ; both conclusions follow directly from our formulas. We therefore obtain for smooth spheres

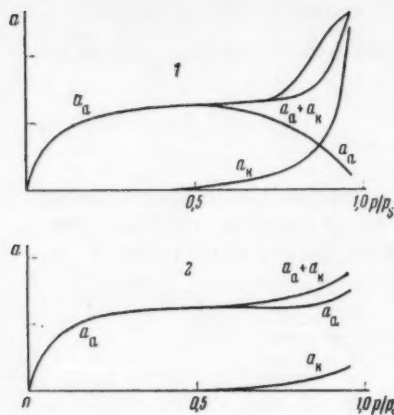
$$a = a_0 + \nu (1/4 \rho_1 / \rho_p U_{11} - a_0 s), \quad (5)$$

where the expression in parentheses may be negative or positive. But in the case of smooth spheres Eq. (3) loses its meaning at  $\nu s > 1$ . The condition  $\nu s = 1$  corresponds to that position of the menisci on the sphere where they touch one another, as a result of which adsorption in general should not occur. Even with not very tight packing this condition is reached at some value of  $p/p_s < 1$ , after which the process enters into a new stage where successive filling by the liquid of the spaces between the spheres lying outside the region of contact occurs. It can be shown easily that when  $\nu = 6$  for benzene, touching of the menisci for particles of  $R = 1 \cdot 10^{-6}$  cm takes place at  $p/p_s \approx 0.95$ . If  $\nu = 12$ , then for  $\beta = 0.8$ ,  $\nu s > 1$  for the same particles, and the boundary position of the menisci, where they touch, approaches that for  $p/p_s = 0.7$ . Consequently for ideally smooth spheres the capillary condensation in the region of still small  $p/p_s$  proceeds by a different mechanism, where Eq. (5) for different menisci is not used; for sufficiently tight packing the part of adsorption in the total sum is very small, as is seen from the formulas.

Another situation occurs in the particles that have some degree of roughness or have an irregularity of a specified type. The factor  $\chi^2$  which enters into Eq. (4) shifts the region of contact of the menisci far in the direction of



large  $p/p_s$  close to  $p/p_s = 1$ , and cases are entirely possible where touching of the menisci and filling up of the spaces between the particles does not occur. Thus at a degree of roughness  $\chi = 0.5$  and  $\nu = 12$  for  $\beta = \infty$  ( $p/p_s = 1$ ) we have  $s_{\infty} = 0.2174$  and then  $\chi^2 \nu s = 0.6522$ , i.e., the surface remains free for adsorption and touching of the menisci does not occur ( $a_a/a_0 = 0.3478$ ). If the roughnesses are relatively small, for example if  $\chi = 0.1$ , then the correction  $\chi^2 \nu s$  in formula (4) in general can be ignored in comparison with unity and adsorption proceeds according to the equation of the adsorption isotherm given for an indefinite surface of a nonporous adsorbent.



Schematic view of isotherms of adsorption ( $a_a$ ) and capillary condensation ( $a_k$ ) for two types of systems: ideal spherical particles (1); rough particles (2).

The considerations stated show that if we limit ourselves to non-porous particles, then we should distinguish two very distinctly expressed types of structure which should lead to two forms of isotherms of sorption consisting of strict adsorption and of capillary condensation. Systems of rough particles where  $R/A \ll 1$  are practically "pure" with respect to adsorption, since for them capillary condensation over almost the whole region of filling may be negligible. These systems should be characterized by the slight dependence of the magnitude of adsorption on packing, i.e., on the average number of contacts per particle. Furthermore, sorption hysteresis, which apparently is due to the complex filling of the voids between the particles, should be very weakly expressed in such systems and may be entirely absent in them.

Systems of smooth spheres or, more accurately, of particles with a negligible degree of roughness are the second type of structure where considerable capillary condensation of vapors may take place along with the sorption process. It is especially noticeable here in the region

of large values of  $p/p_s$ , where the magnitude of the adsorption is greatly decreased because of the decrease in free surface of the particles and the process of capillary condensation, proceeding through the stage of separate menisci, is complicated by their merging and filling of the voids between the particles. In these systems the sorption process should depend greatly on the tightness of packing of the particles; with an increase in the number of contacts the two values  $a_a$  and  $a_k$  increase, as follows from our formulas. In the region of high values of  $p/p_s$  a more or less marked hysteresis should occur in the isotherms. Both types are shown in the schematic Fig. 1. Obviously the possible diversity of the systems is not limited to these types of structures, since various intermediate forms are admissible, and the more so because the determination of the irregularities of the particles introduced by us is neither universal nor accurate. Finally, it is necessary to note the role of compression in preparing samples of sorbents for experiments. Unfortunately insufficient attention has been given to this question up to the present time. However, experimental data [5] and also simple considerations show that even with a rather high density of loose bodies the average value of  $\nu$ , the number of contacts per particle, usually does not exceed 8, but for polydispersed systems it may vary within wide limits. But it still is necessary to have in mind that  $\nu$  is a function of the distribution in a layer and this distribution may prove to be a determining factor in the course of the sorption process, causing specific phenomena [6] in loose bodies. In any case the sorption process in powdery sorbents is rather complex and does not at all permit well defined treatment. We therefore share completely the ideas of Pierce et al. [2] about the uncertainty of the data on thickness of sorption films on free surfaces of sorbents, since these results are based on isotherms for powder samples.

## SUMMARY

1. An evaluation has been given on the adsorption of vapor in systems of contacting particles and general equations have been derived for the adsorption isotherms taking into account the decrease in surface when liquid menisci are formed close to the points of contact.

2. In describing the two processes of adsorption and capillary condensation two types of structures should be differentiated: in one of them the adsorption process is expressed in the purest form where the system consists of rough particles, while in the other the process may be considerably complicated by capillary condensation if the system is obtained by the contact of smooth spherical particles with vanishingly small irregularities. Two forms of sorption isotherms which differ considerably from each other corresponds to these two types.



#### LITERATURE CITED

1. L. V. Radushkevich, *Izv. AN SSSR, Otd. Khim. Nauk* 1961, No. 5.
2. R. T. Davies and T. W. DeWitt, *J. Amer. Chem. Soc.* 70, 1135 (1948); P. C. Carman and F. A. Raal, *Proc. Roy. Soc. A* 209, 59 (1951); J. S. Shereshefsky and E. R. Russel, *J. Phys. Chem.* 57, N 7, 660 (1953); C. Pierce, J. Mool, and R. E. Harris, *J. Phys. Chem.* 62, N 6, 655 (1958).
3. L. V. Radushkevich, *Izv. AN SSSR, Otd. Khim. Nauk* 1952, 1008.
4. B. V. Deryagin, *Dokl. SSSR* 113, No. 4, 842 (1957).
5. W. Smith, P. Foote, and P. Busang, *Phys. Rev.* [2], 34, 127 (1929).
6. L. V. Radushkevich, *Doklady Akad. Nauk SSSR* 57, No. 5, 471 (1947).

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

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# MECHANISM OF CARBON FORMATION IN THE DECOMPOSITION OF METHANE, ETHANE, ETHYLENE AND ACETYLENE ON SILICA GEL

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It was shown earlier [1] from the results of our preceding investigations that the number of possible mechanisms of carbon formation for the decomposition of an organic compound is determined by the number of carbon forming materials of different chemical types which may be both the original materials and the products obtained from their earlier conversion. The change from one mechanism of carbon formation into another is realized when the variation in the conditions is such that one carbon forming material disappears and another appears or where the process of carbon formation from one carbon forming material is inhibited and is dependent on the other. Each mechanism of carbon formation which we studied earlier, represented the process of polycondensation of carbon forming material resulting in the formation of more and more complex polycyclic macromolecules - carboids composing the carbon substance. In the pyrolysis of methane we observed one carbon formation mechanism [1]. In this case, since a certain quantity of ethane, ethylene and acetylene was obtained as well as carbonaceous substance and hydrogen it was of interest to study the process of carbon formation in the decomposition of these hydrocarbons, as well as methane, under comparable conditions and to determine the importance of each of them as a carbon forming material.

## EXPERIMENTAL

The procedure used in the work was the same as that described earlier [1, 2]. The experiments were carried out at atmospheric pressure in a catalytic apparatus, in a flow system, the apparatus containing a detachable quartz reactor. Silica gel (KSM), particle diameter 1-2 mm, used as the charge, was placed in the reactor. In each test 5 ml of fresh silica gel was taken. The carbonaceous material obtained was directly calculated by weighing the reactor with an accuracy of 0.0001 g. The tarry products were collected and quantitatively determined with an accuracy of about 1% of the amount being determined. The rate of evolution of the gaseous products was determined with the aid of a Patrikeev recording gas meter. In each experiment the contact gases were completely analyzed by

means of a chromatographic method, the volumes of the separated components being read visually. The feed velocity of the original hydrogen was about 0.06 mol/hr which was controlled by a flow gauge. The composition of the original hydrocarbons are given in the table.

Composition of Original Hydrocarbons in Volume %

Original hydrocarbons	Components				
	Hydrogen	Methane	Ethane	Ethylene	Acetylene
Methane	0	96	3	1	0
Ethane	traces	0	99.4	0	0
Ethylene	0	0	1.2	98.2	0
Acetylene	0	0	0	traces	99.5

Methane and acetylene were drawn from cylinders of the gases. Ethane and ethylene were synthesized; ethane, by the electrolysis of a solution of sodium acetate with subsequent purification of the gas in the appropriate absorbents and by means of low temperature fractionation; ethylene by the dehydration of ethyl alcohol over aluminum oxide at 400°C followed by purification.

## High Temperature Mechanisms of Carbon Formation

It follows from Fig. 1, that the rate of carbon formation in the decomposition of methane increases smoothly with a rise in temperature and in the same way, the yields of the tarry products increase. The composition of the contact gases also gradually alter (Fig. 2A). These properties are evidence of the existence of only one mechanism of carbon formation in the decomposition of methane as was shown in the earlier investigation [1].

In the case of ethane, ethylene and acetylene, on the contrary, the rates of carbon formation undergo abrupt changes in temperature regions specific for each of these hydrocarbons (cf. Fig. 1A); the yields of the tarry products also pass through maxima at temperature regions specific for each hydrocarbon (Fig. 1B); and the gas composition undergoes sudden intermittent changes in the curves with increase of temperature (Fig. 2B, C, D). In support of this conclusion analogous observations have been reported earlier with a change in the mechanism of carbon formation with the decomposition of alkyl benzenes, naphthenes, higher paraffins and alcohols on catalysts [1-4]. Thus, in the case of ethane, ethylene and acetylene it is possible to take note of two mechanisms of carbon formation: low and high temperature transformation where a change occurs in the following temperature ranges: 875-910°, 810-850°, 620-750° correspondingly.

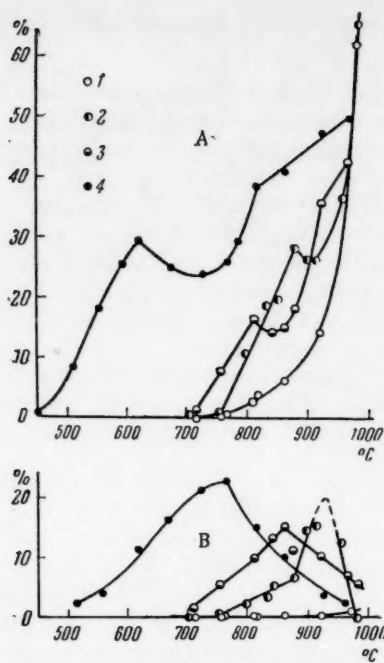


Fig. 1. (A) Variation of carbon formation with temperature and (B) yield of tarry products with temperature (1A, conversion of original hydrocarbons into carbon and 1B into tar, in %) by decomposition on silica gel. 1) Methane; 2) ethane; 3) ethylene; 4) acetylene.

Thus, on the basis of comparing the rates of carbon formation from ethane and methane (cf. Fig. 1A) the proportion of tar as carbon forming material may be approximately estimated as 50% at 910° (lower limit of the high temperature carbon formation) 18% at 950° and 0% at 975°.

In the case of high temperature carbon formation from ethylene and acetylene, methane is also obviously a carbon forming material along with the aromatic tars which is proved by the diminishing proportion of methane in the hydrocarbon part of the contact gases (cf. Fig. 2C and 2D). However, comparison of the rates of carbon formation from these hydrocarbons and from methane in the region of the high temperature mechanism (cf. Fig. 1A) shows

\*The tarry products give very pronounced qualitative reactions for aromatics with concentrated sulphuric acid; they give a green fluorescence in benzene solutions — a property of condensed aromatics; the major constituents in certain cases is naphthalene separated from the tar by crystallization and identified by its melting point in the pure form and by the mixed melting point. The presence of different condensed aromatic hydrocarbons: naphthalene, diphenyl, phenanthrene, anthracene etc., in the tarry products from the pyrolysis of the compounds which we investigated, has been reported earlier in numerous investigations [5-11 and others].

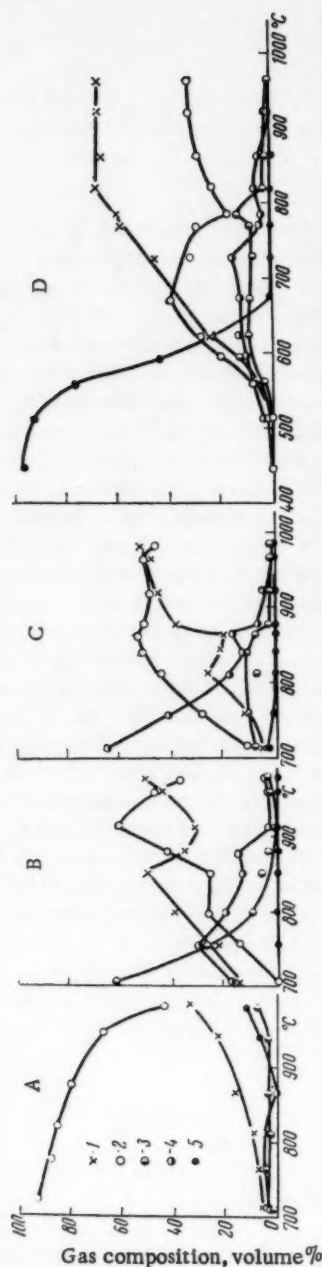
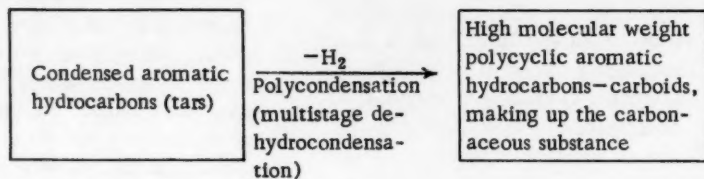


Fig. 2. Composition of contact gases (in volume %) in the decomposition of methane (A), ethane (B), ethylene (C) and acetylene (D) on silica gel. Constituents of the contact gases: 1) hydrogen; 2) methane; 3) ethylene; 4) ethylene; 5) acetylene.

that the proportion of tar as the carbon forming material in the case of ethylene and acetylene is significantly more than in the case of ethane. Thus, at 750° for acetylene it equals 98%; at 850° for ethylene it equals 64% and for acetylene 87%; at 950° it equals 27% for ethylene and it equals 39% for acetylene. Thus, it is clear that the proportion of tar in high temperature carbon formation increases in a series of hydrocarbons as starting materials — ethane, ethylene, acetylene, and it decreases with an increase in temperature.

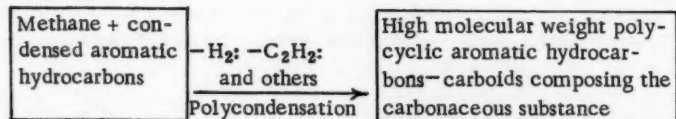
In the case of methane obviously only high temperature mechanism of carbon formation occurs — with the carbon forming material being methane. The aromatic tars in this case evidently play almost no part as a carbon forming material. This is confirmed by the insignificant rate of their formation compared with the rate of carbon formation and the even increase in the yield of tars with an increase of temperature and of the rate of carbon formation (cf. Fig. 1, A and B), as distinct from the fall in the tar yields in the region of the high temperature mechanism of carbon formation in the decomposition of the hydrocarbons — ethane, ethylene and acetylene used as starting materials, when the tars are consumed as the carbon forming material. Thus, in all the cases considered either the aromatic tars and methane are the carbon forming materials or methane alone.

The formation of carbonaceous material from aromatic tars by the high temperature mechanism is easily presented in the form of a multi-stage process of the dehydrocondensation of aromatic hydrocarbons; naphthalene, phenanthrene, and anthracene, tetracene and others, the constituents being available in the form of tar, analogous to the multi-stage process of the dehydrocondensation of benzene [12]. In this way, by the elimination of hydrogen, more and more condensed polycyclic macromolecules of hydrocarbons — carboids are obtained, present in the composition of the carbonaceous material (cf. flow sheet).



The increase in the hydrogen concentration in the contact gases and the decrease in yield of tars with increase in temperature confirm that this picture of the mechanism is correct.

The formation of carbonaceous material directly from methane by the high temperature mechanism may be presented as the multi-stage dehydrocondensation of methane with the carbonaceous substance and aromatic tars. In this case, when the aromatic tars cannot ensure that carbon formation occurs by acting as the carbon forming material, then their importance in the process is reduced to being the nuclei of the macromolecules of the carbonaceous substance with which the dehydrocondensation of methane also occurs (cf. scheme).





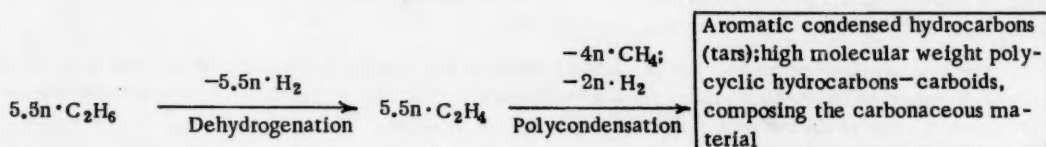
The preliminary formation of the aromatic condensed hydrocarbons, required as the nuclei, obviously occurs due to the conversion of the methane into ethane and ethylene which in fact are present in the contact gases beginning from a temperature of 700° (cf. Fig. 2A). The formation of ethane and ethylene from methane at comparatively low temperatures has also been reported by other authors [10, 13]. It is of interest to note that acetylene, which only appears in the decomposition products of methane at a temperature above 875° (cf. Fig. 2A), in this case, cannot be considered as a possible tar forming and carbon forming material, but is in fact a secondary product of the carbon formation. The concentration of acetylene increases with an increase of temperature, while, if the examples of the decomposition of ethane, ethylene and acetylene used as starting materials are considered, it can be seen that acetylene cannot be obtained in the free form in contact gases at temperatures above 800° but is completely converted into carbonaceous substance and tar (cf. Fig. 2B, C, D). A possible explanation of this fact may be that acetylene (and hydrogen) is liberated in the polycondensation process of methane with carbonaceous material and that the polycondensation of acetylene with the carbonaceous substance because of energy considerations is less favored at high temperatures than the polycondensation of methane. There are certain facts known which are in accord with this explanation, namely the increase in the concentration of acetylene with increase in the pyrolysis temperature of methane [11, 14].

#### Low Temperature Mechanisms of Carbon Formation and Production of Aromatic Tars.

In the decomposition of ethane, ethylene and acetylene by the low temperature mechanism of carbon formation, the aromatic tars are obviously not the carbon forming material because a noticeable consumption of tars in carbon formation is only observed when the high temperature mechanisms of carbon formation come into force. An increase of temperature in the regions where the low temperature mechanisms of carbon formation operate, brings about a simultaneous increase in the rate of tar formation and carbon formation (cf. Fig. 1A and 1B), which indicates the parallelism of these processes. Comparison of the rates of carbon formation from ethane and ethylene and the composition of the gaseous products in the region of low temperature mechanisms of carbon formation (cf. Fig. 1A and Figs. B and C) show that the carbon forming material here is ethylene, previously obtained from ethane or the original stock. In fact, in practice, no carbon formation from ethane occurs before 750° until the concentration of ethylene in the gases is increased to 30-35% (cf. Fig. 1A and 2B). At the same time, in the case of ethylene as the starting material carbon is deposited at a high rate, beginning from 700° (cf. Fig. 1A). The same phenomenon is observed for tar formation from ethane and ethylene (Fig. 1B). Thus, only in the presence of a determined concentration of ethylene in the gases will an increase of temperature cause a significant increase in the rate of carbon and tar formation both occurring together by similar mechanisms with only one material, ethylene, being the carbon and tar forming material. The concentration of ethane, obtained from ethylene as starting material is a constant value (approximately 10%) in all regions of the low temperature mechanism and consequently in both cases ethane is obviously not the carbon forming material. It is also necessary to consider the case of acetylene to reach the same conclusion about the processes occurring in carbon formation since it is completely absent in the decomposition product of ethane and is found in insignificant quantities in the decomposition products of ethylene (cf. Fig. 2C, and 2D).

In the low temperature region of carbon formation from ethane and ethylene increased concentrations of hydrogen and methane are found in the contact gases. Moreover it is necessary to consider the fact that the concentrations of these products are comparable and significant and that their yields increase together with increase of temperature, indicating that an increase in the yields of the carbonaceous material and tars occurs (cf. Fig. 1A and 1B, 2C and 2D). Obviously, this type of relation occurs because both methane and hydrogen to a significant extent are obtained in the process of polycondensation of ethylene, leading to the carbonaceous material and tars. As concerns hydrogen, its loss in carbon formation processes in the decomposition of hydrocarbons is a usual phenomenon. The release of methane in the carbon formation process is a rarer case; we observed this in the polycondensation of propylene obtained from isopropyl alcohol at 600-775° [15]. The case under consideration of low temperature carbon formation from ethane and ethylene represents only one example when the loss of methane occurs together with dehydrogenation.

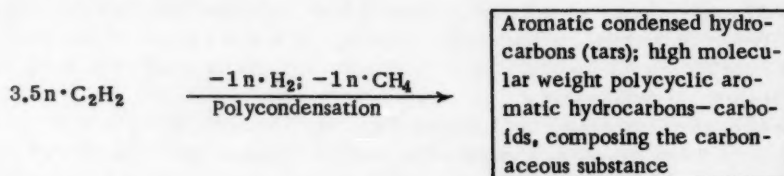
From the results obtained, the process of low temperature carbon formation and the production of aromatic tars in the decomposition of ethane and ethylene may be represented by the following flow sheet:





It follows from the analysis of the results represented in Fig. 1A, 1B and 2D that the acetylene stock itself is the carbon and tar forming material in the decomposition of acetylene by the low temperature mechanism. The increase in the rate of carbon formation with increase of temperature occurs only at temperature less than 620° when the acetylene concentration in the gases decreases to 25%. Above 620° the transitional region between the low and the high temperature mechanisms with inhibition of carbon formation begins. No effect on the rate of increase of tar yield is revealed at this temperature limit (620°); the tar yields continue to increase to 750° up to an upper temperature limit of the transitional region. This difference in the shape of the curves of the rates of carbon and tar formation from the one material is evidence that direct polycondensation of acetylene into carbonaceous material by the low temperature mechanism is only possible at its higher concentrations, but the polycondensation of acetylene into aromatic tars is also possible with insignificant concentrations of free acetylene. Consequently, above 675° when free acetylene is completely absent in the contact gases (cf. Fig. 2D) any acetylene which is injected into the reaction is converted into aromatic tars. In other words, if each polycyclic molecule of tar is considered as the nucleus of a new macromolecule of the carbonaceous material, then by reducing the concentration of the free acetylene below 25% the formation of new nuclei proceeds more rapidly than the growth of each of them. Just as in the case of ethane and ethylene, in the mechanism of low temperature carbonization from acetylene the variation in the rates of carbon and tar formation and in the increase of the concentration of methane and hydrogen in the contact gases proceed in parallel (cf. Fig. 1A, 1B and 2D). The concentrations of ethane and ethylene in the same temperature region are not high and as distinct from the methane and hydrogen are practically constant (cf. Fig. 2D). Obviously, in this case also methane and hydrogen are obtained in the process of polycondensation of acetylene leading to the formation of aromatic tars and the carbonaceous substance.

The process of low temperature carbon formation and the production of aromatic tars on the decomposition of acetylene on silica gel may be given in the following flow sheet:



With increase of temperature prior to the transitional region to the high temperature mechanism of carbon formation, the conditions for removal of methane in the polycondensation processes of ethylene and acetylene obviously become unfavorable and the methane itself acquires the capacity to be dehydrocondensed with the carbonaceous material which results in a decreased concentration of methane and an increase in the concentration of hydrogen in the contact gases (cf. Fig. 2B, 2C, 2D). The polycondensation of methane which is obtained with aromatic tars and carbonaceous material in the high temperature mechanism of carbon formation is a complete vindication of the theory which has been proposed. A certain gradual transition from the low temperature mechanism of carbon formation to the high temperature mechanism is also characterized by the fact that in the transitional regions of carbon formation in the decomposition of ethane, ethylene and acetylene the process has a considerable tendency to take place with the tar being the carbon forming material. This feature is noticeable in the case of acetylene when there is 100% carbon formation at the upper limit of the transitional region due to the polycondensation of the aromatic tars.

#### SUMMARY

1. The existence of one mechanism of carbon formation in the decomposition of methane (over the range 450-1000°) has been confirmed and the existence of two mechanisms of carbon formation (low temperature and high temperature) in the cases of the decomposition of ethane, ethylene and acetylene has been shown.
2. The high temperature mechanism of carbon formation represents the polycondensation of the previously obtained aromatic tars and methane. The proportion of the tar fraction as the carbon forming material in comparison with methane increases in a series of hydrocarbons used as starting materials (i.e., methane, ethane, ethylene and acetylene) and decreases with increase of temperature.
3. The low temperature mechanism of carbon formation and also the mechanism of tar formation represents the polycondensation of the original, or previously obtained, ethylene and acetylene. These processes occur in parallel and include a stage of dehydrogenation and the removal of methane.

# LITERATURE CITED

1. A. P. Rudenko, A. A. Balandin, and Yu. Chueva, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* 1961, 164.
2. A. P. Rudenko, A. A. Balandin, and I. I. Grashchenko, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* 1960, 605.
3. A. P. Rudenko, A. A. Balandin, and S. Ya. Kachan, *Izv. Akad. Nauk* 1960, 981.
4. G. Stegner, A. P. Rudenko, and A. A. Balandin, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* 1960, 1930.
5. K. Norton and M. Noyes, *Amer. Chem. J.* 8, 362 (1886).
6. W. A. Bone and H. F. Coward, *J. Chem. Soc.* 93, 1197 (1908).
7. R. Meyer, *Ber.* 45, 1609 (1912).
8. N. Zelinsky, *Ber.* 57, 264 (1924).
9. R. V. Wheeler and S. Wood, *Fuel Science Pract.* 7, 535 (1928).
10. E. N. Hague and R. V. Wheeler, *J. Chem. Soc.* 1929, 378.
11. Symposium "Cracking of Hydrocarbons" [in Russian] ONTI (United Scientific and Technical Press), Moscow - Leningrad (1935).
12. A. P. Rudenko, *Vestn. Mosk. Univ. seriya khim* 5, 69 (1960).
13. H. H. Storch, *J. Amer. Chem. Soc.* 54, 4188 (1932).
14. N. I. Kobozev, L. I. Kashtanov, and S. M. Kobrin, *Zhur. Obshch. Khimii* 5, 143 (1935).
15. A. A. Balandin, A. P. Rudenko, and G. Stegner, *Doklady Akad. Nauk SSSR* 129, 3, 565 (1959).

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

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## DECOMPOSITION OF ISOPROPANOL ON ALUMINA-CHROMIUM CATALYSTS

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We have undertaken an investigation of the effect of component ratio and thermal treating conditions on the catalytic properties of  $\text{Al}_2\text{O}_3\text{-Cr}_2\text{O}_3$ , in an expansion of analogous studies with  $\text{NiO-Al}_2\text{O}_3$  [1] and  $\text{Fe}_2\text{O}_3\text{-Al}_2\text{O}_3$  [2] which were conducted with isopropanol and which made it possible to reveal and explain specific features of the behavior of these systems on the basis of determining their phase composition and structure [3, 4]. As is well known, alumina-chromium catalysts are utilized not only for alcohol decomposition, but also for condensation reactions of acetaldehyde with ethanol, dehydrocyclization of paraffins, dehydrogenation of alkylbenzenes and paraffins, and several other processes. These fields of application have been taken up in recently published reviews [5, 6] covering all of the basic literature on alumina-chromium catalysts. The phase composition of alumina-chromium was first established very recently [7]. No determination of specific activity has been performed in any of the work with  $\text{Cr}_2\text{O}_3\text{-Al}_2\text{O}_3$ . This also was one of the tasks of the present work. A second task was the characterization of the selectivity of action in the two parallel reactions of dehydrogenation and dehydration. A structural investigation was conducted simultaneously, described in more detail in another communication [8]; here we utilize only the data on the magnitudes of specific surface. Let us note also that it was necessary to obtain data on the specific activity of the  $\text{Al}_2\text{O}_3\text{-Cr}_2\text{O}_3$  to evaluate the influence of  $\text{K}_2\text{O}$  in  $\text{K}_2\text{O}$ -promoted alumina-chromium catalysts, the specific activity and structure of which had been determined previously in our laboratory [9].

### EXPERIMENTAL

All of the catalysts were prepared from a single batch of the original salts (ch.d.a.) [analytically pure]. A solution of weighed amounts of aluminum and chromium nitrates in distilled water was brought to a volume of 1.5 liters, and the hydroxides were precipitated at room temperature with vigorous stirring, slowly adding the calculated amount of 10% ammonia solution. The precipitate was allowed to stand for one day, after which the solution pH was determined (LP-5 potentiometer). The precipitate was washed 4-5 times by decantation and centrifuged, and then was vacuum-filtered on a Buchner funnel, formed by pressing through dies, dried in air for one day, and then dried in a drying cabinet at  $110^\circ$ . Individual portions of the hydroxide mixture of each composition were calcined at  $450$  and  $600^\circ$  for six hours, cooled in a desiccator, and stored under conditions preventing moisture access. For determining the "residual" water\* small weighed samples were calcined at  $1000\text{-}1100^\circ$  for six hours. The size of the calcined catalyst grains varied between 1 and 3 mm in length with a diameter of 1 mm. Analysis (iodometric) of the catalysts for  $\text{Cr}_2\text{O}_3$  content gave good agreement with the calculated compositions. The method described was also used to make preparations of the catalyst components, pure  $\text{Al}_2\text{O}_3$  and  $\text{Cr}_2\text{O}_3$ . The investigations of the phase composition and texture of the catalysts that were prepared was described in [8]; the determination of the magnitudes of the specific surface in this work was carried out by measuring benzene vapor adsorption at  $20^\circ$  on a MacBain balance. These magnitudes are shown in Table 1 along with other characteristic properties of the catalysts prepared. In the catalysts containing  $\text{Cr}_2\text{O}_3 > 25\%$  a rapid decrease occurs in the magnitude of specific surface and residual water content ( $450^\circ$  series).

The experiments were conducted with absolute  $\text{i-C}_3\text{H}_7\text{OH}$ ,  $n^{20}_D$  1.3775. The determination of activity was carried out through 4-5 experiments at the given space velocity and temperature in the range of  $245\text{-}320^\circ$  in  $15^\circ$  intervals, returning after each cycle to a lower temperature, and also through 2-3 experiments on a fresh sample at another space velocity. In those cases in which the degree of conversion was very high, no experiments were

\* These data are approximate, since part of the weight losses is caused by splitting off oxygen from the chromates formed in the thermal treatment.

conducted at the higher temperatures. With pure chromic oxide (samples I-III) experiments were conducted at higher temperatures, owing to its low activity at the low temperatures. The experimental data on the determination of activity are shown in Tables 2 and 3. The method of obtaining these data (flow system) was the same as in [1, 2, 9]. In all experiments the catalyst volume was 2 cm<sup>3</sup>. The alcohol feed space velocities were 2.3 and 3.2 hr<sup>-1</sup> for the series of catalysts calcined at 450°, and 2.1 and 3.5 hr<sup>-1</sup> for those calcined at 600°. The catalyst containing 75% Cr<sub>2</sub>O<sub>3</sub> and calcined at 600° was also used in conducting experiments at a space velocity of 6.2 hr<sup>-1</sup>. In all experiments, before starting the measurements, the gas was displaced from the apparatus by the products of i-C<sub>3</sub>H<sub>7</sub>OH decomposition at the test temperature for 0.5-1.5 hr, depending on the catalyst activity. The reaction rate was judged by the volumes of propylene and hydrogen, reduced to normal conditions (NTP). The gases were analyzed in a VTI-2 apparatus. In addition to C<sub>3</sub>H<sub>6</sub> and H<sub>2</sub>, the gas mixture contained small (0.2-0.4%) quantities of CO<sub>2</sub>. No significant carbonization of the samples was observed. The reproducibility of the experiments in the 600° series was somewhat better than in the 450° series. In the majority of cases the divergence between the first experiment and the repeats did not exceed 10% of the values obtained in the first experiment.

Certain catalysts (3, 15, and 100% Cr<sub>2</sub>O<sub>3</sub>) were prepared with differing final pH values in the precipitation. The properties of these preparations at a given Cr<sub>2</sub>O<sub>3</sub> concentration [with varying pH] differ markedly, as is evident from Tables 1-3.

TABLE 1. Characteristic Properties of Catalysts Investigated

Cr <sub>2</sub> O <sub>3</sub> content, mole%	pH of precipitation	Residual water, %		Bulk density (600° series) g/cm <sup>3</sup>	Specific surface, g/cm <sup>3</sup>	
		450°	600°		450°	600°
0(Al <sub>2</sub> O <sub>3</sub> )	6,8	3,4	0,9	0,82	200	190
1,0	7,6	3,9	1,2	0,73	282	204
3,0 (I)	6,4	4,0	2,1	0,85	217	221
3,0 (II)	7,6	4,9	2,0	—	260	256
5,0	7,1	4,2	3,2	0,65	309	297
10,0	7,0	5,0	3,0	0,82	288	312
15,0 (I)	7,5	3,8	3,4	0,54	298	255
15,0 (II)	6,7	6,1	2,0	0,73	284	320
25,0	7,4	6,2	1,5	0,92	261	241
50,0	6,8	2,9	1,5	0,94	240	142
75,0	7,4	2,4	1,4	0,98	103	66
90,0	6,8	1,2	1,4	1,00	32	28
100,0 (I)	8,8	1,0	1,2	0,57	20	29
100,0 (II)	7,0	1,1	1,0	1,15	16	
100,0 (III)	8,0	1,4	1,6	1,02	21	14

#### Discussion of Experimental Results

As is evident from Table 1, the catalysts of both series contained a varying quantity of residual water. A comparison of residual water content vs. catalyst composition is made in Fig. 1. It shows in general a similar path of the curves for the series of catalysts calcined at 450 and 600°, the water content in the 450° catalysts being approximately double that in the 600° catalysts except at high Cr<sub>2</sub>O<sub>3</sub> contents, where this difference disappears completely. From Fig. 1, it is evident that the sharpest change in residual water content takes place at a high Al<sub>2</sub>O<sub>3</sub> content and that there is a distinct maximum in the curves near 15% Cr<sub>2</sub>O<sub>3</sub> (85% Al<sub>2</sub>O<sub>3</sub>); this maximum is evidently caused primarily by the dependence of specific surface on catalyst composition, as evidenced by comparing the shape of the curves in Fig. 1, with the data of Table 1: The specific surface also passes through a maximum in the region of 10-20% Cr<sub>2</sub>O<sub>3</sub>. On the basis of these analogous changes, it can be presumed that the residual water in the catalysts is concentrated mainly at the surface, and that this is chemisorbed water, forming surface OH groups, thus explaining the difficulty of its removal from the catalysts.

The magnitudes of the reaction rate constants were calculated by the Balandin-Bork equation [10]

$$k = \frac{N \cdot m}{M - m/2}$$

from the data of all the experiments. These magnitudes, which are shown in Table 4, were used for calculating catalyst specific activities. However, in view of the high degree of conversion (> 30-35%) in a number of experiments,



the constants calculated from the data of these experiments are only approximate nominal values. The corresponding magnitudes are shown in Table 4 in bold-face type; they were not utilized in calculating the magnitudes of activation energy for the reactions.

TABLE 2. Activity of Catalysts Calcined at 450°

Cr <sub>2</sub> O <sub>3</sub> content in catalyst	245°		260°		275°		290°		305°		320°	
	C <sub>3</sub> H <sub>6</sub>	H <sub>2</sub>	C <sub>3</sub> H <sub>6</sub>	H <sub>2</sub>	C <sub>3</sub> H <sub>6</sub>	H <sub>2</sub>	C <sub>3</sub> H <sub>6</sub>	H <sub>2</sub>	C <sub>3</sub> H <sub>6</sub>	H <sub>2</sub>	C <sub>3</sub> H <sub>6</sub>	H <sub>2</sub>
0(Al <sub>2</sub> O <sub>3</sub> )	100	0	174	0	245	0	—	—	—	—	—	—
	34		60		84							
1	—	—	93	0	167	0	219	0	—	—	—	—
			32		58		75					
3 (I)	41	0	96	0	182	0	240	0	—	—	—	—
	14		33		62		82					
3 (II)	44	0	89	0	186	0	255	0	—	—	—	—
	15		30		64		87					
5	—	—	76	3,5	113	2,3	178	2,0	—	—	—	—
			26	1,2	38	0,7	61	0,6				
10	—	—	39	3,8	88	7,6	165	6,9	—	—	—	—
			13	1,3	30	2,6	56	2,3				
15 (I)	—	—	57	5,1	118	6,0	186	8,3	—	—	—	—
			19	1,7	40	2,0	63	2,7				
15 (II)	—	—	—	—	62	10,1	103	13,8	164	17,0	—	—
					21	3,5	35	5,0	56	6,0		
25	—	—	—	—	45	8,4	102	12,7	167	19,0	—	—
					15	2,8	35	4,0	57	6,4		
50	—	—	—	—	26	17,2	80	22,8	133	19,8	—	—
					9	5,8	27	7,7	45	7,0		
75	—	—	—	—	23	22,0	42	21,0	73	33,6	—	—
					8	7,6	14	7,0	25	11,0		
90	—	—	—	—	—	—	32	30	53	32	85	40
							11	10	18	11	29	13
100 (I)	—	—	—	—	—	—	—	—	—	—	46	44
											16	15
100 (II)	—	—	—	—	—	—	—	—	—	—	50	60
											17	20
100 (III)	—	—	—	—	—	—	—	—	—	—	54	72
											18	25

Note: In this and the following tables the upper line for each catalyst shows the volumes of C<sub>3</sub>H<sub>6</sub> and H<sub>2</sub> (in ml NTP) formed per ml of alcohol throughout. The lower line represents the degree of conversion in percent.

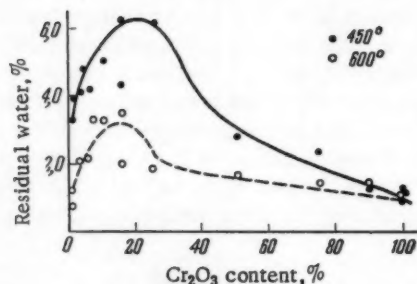


Fig. 1. Variation in residual water content in alumina-chromium catalysts depending on composition.

The values obtained for reaction rate constants for both series of catalysts with degrees of conversion up to 30-35% are approximately proportional to the degrees of conversion (compare Tables 2, 3, 4). At the indicated degrees of conversion the dehydration reaction rate is independent of the alcohol feedstock space velocity. It was shown by special experiments using the 75% Cr<sub>2</sub>O<sub>3</sub> catalyst calcined at 600° that the propylene yield at 275 and 290° remains constant (within the limits of error) with a change in space velocity from 2.1 to 6.2 hr<sup>-1</sup>. When 320° is reached, the propylene yield increases with an increase in space velocity. Thus, in our experiments a zero order of reaction is observed for the dehydration reaction at degrees of conversion up to 30-35%. For the dehydrogenation reaction this relationship is less clearly expressed, apparently in view of the low degrees of conversion in this direction in the majority of the experiments and the consequently larger error of the experiments and the analytical determinations.

The catalyst containing 75% Cr<sub>2</sub>O<sub>3</sub> was used in conducting a series of experiments to ascertain the influence of grain size, i.e., the influence of diffusion, on the reaction rate. Experiments conducted at 275 and 310° with



catalyst grains (1) length 3 mm, diameter 1 mm (2) length 1 mm, diameter 1 mm, and (3) 0.1-0.3 mm particles showed that the reaction rates were identical in these three cases; hence, it follows that our basic experiments were conducted in the kinetic region.

TABLE 3. Activity of Catalysts Calcined at 600°

Cr <sub>2</sub> O <sub>3</sub> content in catalyst	260°		275°		290°		305°		320°		335°	
	C <sub>3</sub> H <sub>6</sub>	H <sub>2</sub>	C <sub>3</sub> H <sub>6</sub>	H <sub>2</sub>	C <sub>3</sub> H <sub>6</sub>	H <sub>2</sub>	C <sub>3</sub> H <sub>6</sub>	H <sub>2</sub>	C <sub>3</sub> H <sub>6</sub>	H <sub>2</sub>	C <sub>3</sub> H <sub>6</sub>	H <sub>2</sub>
0(Al <sub>2</sub> O <sub>3</sub> )	164	0	225	0	293	0	—	—	—	—	—	—
	56	—	77	—	100	—	—	—	—	—	—	—
3	—	—	190	3,1	220	—	258	—	293	—	—	—
	—	—	65	1,0	75	—	88	—	100	—	—	—
3 (II)	—	—	196	2,8	230	1,7	270	—	289	—	—	—
	—	—	67	1,0	79	0,6	92	—	99	—	—	—
5	74	3,2	142	2,3	213	2,4	253	—	291	—	—	—
	25	1,1	48	0,8	73	0,8	86	—	99	—	—	—
10	—	—	—	—	157	4,1	213	4,8	235	3,7	—	—
	—	—	—	7,1	53	1,4	73	1,6	80	1,2	—	—
15	—	—	90	2,4	119	7,6	155	4,3	186	4,8	—	—
	—	—	31	—	41	2,6	53	1,5	69	1,6	—	—
15 (II)	—	—	—	—	115	12,1	145	12,5	167	9,7	—	—
	—	—	—	—	39	4,1	50	4,3	57	3,3	—	—
25	—	—	42	14,4	95	14,4	149	16,0	204	22,6	—	—
	—	—	14	4,9	32	4,9	51	5,4	71	7,7	—	—
50	—	—	43	13,2	94	9,7	146	11,8	205	8,2	—	—
	—	—	14	4,5	32	3,3	50	4,1	71	2,8	—	—
75	—	—	17,4	11,0	49	10,7	75	35,0	135	40,2	191	20,1
	—	—	5,9	3,8	16	3,7	25	12,0	46	13,7	65	6,8
90	—	—	13,6	11,5	28,0	19,4	52,0	21,0	72	41,0	107	46,0
	—	—	4,6	3,9	9,5	6,6	17,7	7,0	24	14,0	36	15,6
100 (III)*	—	—	—	—	—	—	—	—	45,8	57,3	—	—
	—	—	—	—	—	—	—	—	15,6	19,9	—	—

\* The Cr<sub>2</sub>O<sub>3</sub> samples I, II, and III were also tested at 350°, giving degrees of conversion (respectively): C<sub>3</sub>H<sub>6</sub> 15,8, 27,5, and 25,6%; H<sub>2</sub> 18,1, 30,1, and 30,0%.

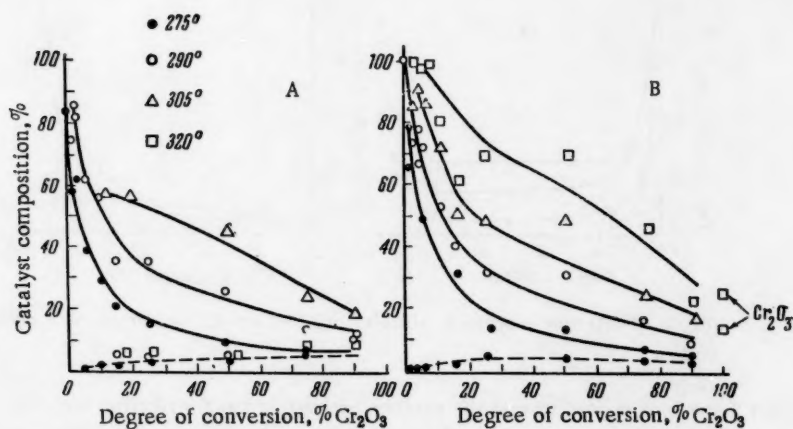


Fig. 2. Dependence of degree of conversion on composition of Al-Cr catalysts: A) 450° series; B) 600° series. Solid curves—dehydration; dashed curves—dehydrogenation.

The magnitudes of the apparent activation energy of dehydration calculated from the rate constants by the Arrhenius equation change only slightly on going from the 450° series to the 600° series or on varying the catalyst composition within each series, and on the average are equal to 27-28 kcal/mole for the 450° series and 32 kcal/mole for the 600° series. This magnitude which we found for the activation energy of isopropanol dehydration on alumina-chromium catalysts is somewhat lower than that determined for the same reaction on pure chromic oxide (II).

TABLE 4. Magnitudes of Rate Constants for Dehydration and Dehydrogenation of Isopropanol ( $k \cdot 10^{-4}$ ) on Catalysts Calcined at 450° (first line in each square) and at 600° (second line)

Cr <sub>2</sub> O <sub>3</sub> in cata- lyst, %	245°		260°		275°		290°		305°		320°	
	C <sub>3</sub> H <sub>8</sub>	H <sub>2</sub>	C <sub>3</sub> H <sub>8</sub>	H <sub>2</sub>	C <sub>3</sub> H <sub>8</sub>	H <sub>2</sub>	C <sub>3</sub> H <sub>8</sub>	H <sub>2</sub>	C <sub>3</sub> H <sub>8</sub>	H <sub>2</sub>	C <sub>3</sub> H <sub>8</sub>	H <sub>2</sub>
0 (Al <sub>2</sub> O <sub>3</sub> )	3,9	—	8,1	—	13,6	—	—	—	—	—	—	—
1	3,9	—	7,2	—	11,5	—	18,5	—	—	—	—	—
3	—	—	3,6	—	7,7	—	11,3	—	—	—	—	—
3 (II)	—	—	—	—	8,9	0,1	11,7	—	14,6	—	18,4	—
5	1,4	—	3,8	—	8,5	—	13,0	—	—	—	—	—
10	1,6	—	3,4	—	8,9	—	14,5	—	—	—	—	—
15	—	—	—	—	9,3	0,09	11,9	0,05	15,7	—	17,8	—
15 (II)	—	—	2,8	—	4,6	0,07	8,2	0,06	—	—	—	—
25	—	—	2,7	0,1	5,9	0,07	10,5	0,08	14,0	—	18,2	—
50	—	—	1,4	0,1	3,4	0,26	7,5	0,23	—	—	—	—
75	—	—	—	0,13	—	—	6,7	0,13	10,5	0,15	12,4	0,15
90	—	—	2,0	—	4,8	0,2	8,8	0,27	—	—	—	—
100	—	—	—	0,17	3,3	0,23	4,7	0,24	6,6	0,14	8,6	0,15
100 (II)	—	—	—	—	2,2	0,34	4,1	0,56	7,5	0,58	—	—
100 (III)	—	—	—	—	—	—	4,4	0,39	6,1	0,40	7,3	0,31
100 (IV)	—	—	—	—	—	—	4,7	0,4	7,6	0,64	—	—
100 (V)	—	—	—	—	1,4	0,46	3,6	0,46	6,3	0,52	9,9	0,74
100 (VI)	—	—	—	—	0,9	0,58	3,1	0,78	5,6	0,68	—	—
100 (VII)	—	—	—	—	1,4	0,42	3,4	0,76	6,1	0,38	9,9	0,26
100 (VIII)	—	—	—	—	0,8	0,77	1,5	0,72	2,7	1,18	—	—
100 (IX)	—	—	—	—	0,6	0,35	1,7	0,34	2,7	1,17	5,7	1,36
100 (X)	—	—	—	—	—	—	1,1	1,03	1,9	1,12	3,3	1,42
100 (XI)	—	—	—	—	0,4	0,37	0,9	0,63	1,8	0,68	2,6	1,32
100 (XII)	—	—	—	—	—	—	—	—	—	—	1,7	1,5
100 (XIII)	—	—	—	—	—	—	—	—	—	—	—	—
100 (XIV)	—	—	—	—	—	—	—	—	—	—	1,8	2,18
100 (XV)	—	—	—	—	—	—	—	—	—	—	1,8	2,00
100 (XVI)	—	—	—	—	—	—	—	—	—	—	1,8	2,50

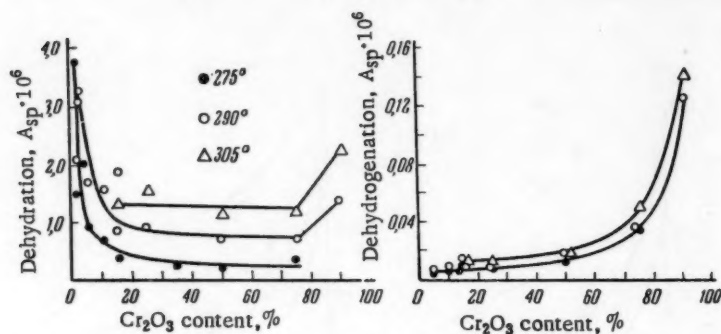


Fig. 3. Variation in specific activity of Al-Cr-450° catalysts with composition.

From Tables 2 and 3, it is evident that the catalyst activity in the dehydration reaction, the same as the total activity with respect to both reactions, at each of the temperatures increases with an increase in aluminum oxide content over the entire interval of catalyst component concentrations which were studied. Deviations from this relationship are of a random nature. The activity in the dehydrogenation reaction shows a slight increase with an increase in chromic oxide content in the mid-range and a sharper increase at higher Cr<sub>2</sub>O<sub>3</sub> concentrations. No activating influence of minor additions of chromic oxide on the dehydrating activity of alumina is observed in the alumina-chromium catalysts; on the contrary, a marked reduction in activity occurs. For each of the reactions the course of the change in activity (degree of conversion) with catalyst composition is in general identical for both series (450 and 600°), as is evident from Fig. 2. It also shows that with an increase in alcohol decomposition temperature the dehydration is intensified to a significant extent, in particular in the catalysts containing 25-75% Cr<sub>2</sub>O<sub>3</sub>, but the dehydrogenation (see 450° series; for the 600° series the differences are still less) remains at practically a single level.

There is a completely different variation in the specific activity of the catalysts, calculated as the ratio of reaction rate constant to the magnitude of the surface of the catalyst (Figs. 3 and 4); in the dehydrogenation reaction the specific activity in general increases evenly with an increase in chromic oxide content of the catalyst, but in the dehydration it has a minimum which is highly extended in the case of the 450° series and localized at 15-25 mole%  $\text{Cr}_2\text{O}_3$  in the case of the 600° series. Comparing this result with the data of the phase analysis of the catalysts [8], it can be stated that both in the 450° series and in the 600° series the decrease in specific activity in the dehydration reaction parallels an increase in the content of chromic oxide in solid solution in aluminum oxide, having a spinel structure, right up to the content corresponding to a saturated solid solution. Here three factors may show influence: (a) a change in semiconductor properties with an increase in  $\text{Cr}_2\text{O}_3$  content (we have started to examine the role of this factor), (b) an increase in the lattice parameter of the spinel phase with an increase in  $\text{Cr}_2\text{O}_3$  content, and (c) an increase in the distance between aluminum ions on the catalyst surface with an increase in the concentration of Cr ions. The second of these geometrical factors (c) may have a stronger influence than the first (b), since all of our experiments showed that the dehydrating activity of the mixed catalysts is lower than that of aluminum oxide prepared by an analogous method.

The increase in dehydrating specific activity for the 450° series catalysts starts only with a  $\text{Cr}_2\text{O}_3$  content of 75%, but for the catalysts calcined at 600° this increase occurs more sharply and immediately after the  $\text{Cr}_2\text{O}_3$  content passes beyond the limits of its concentration in the spinel-structure saturated solid solution. The difference in behavior of the catalysts calcined at 450 and 600° can be explained by the fact that with  $\text{Cr}_2\text{O}_3$  content above 20 wt. % there appears chromic oxide and a solid solution of aluminum oxide in it, having a corundum structure. In the 450° series such a crystalline phase appears only beginning with 50%  $\text{Cr}_2\text{O}_3$  in the catalysts, whereas in the 600° series it is shown quite distinctly [8] by the time the  $\text{Cr}_2\text{O}_3$  content has reached 25% and is crystallized far better than in the preparations of the 450° series. Apparently precisely this circumstance is also the reason why the minimum in specific activity for this series of preparations is so markedly extended. Beyond the limits of 20%  $\text{Cr}_2\text{O}_3$  the spinel and corundum phases coexist and act simultaneously. The more rapid increase of corundum phase concentration in the catalysts calcined at 600° leads to a more rapid increase of specific activity after the minimum. From this it follows that in the decomposition of isopropanol the dehydrating activity of the  $\text{Cr}_2\text{O}_3$ -rich corundum phase exceeds that of the spinel-structure saturated solid solution. It should also be added that on increasing the temperature of the alcohol decomposition the steepness of the rise in the branches of the curves after the minimum (Figs. 3 and 4) is increased very markedly.

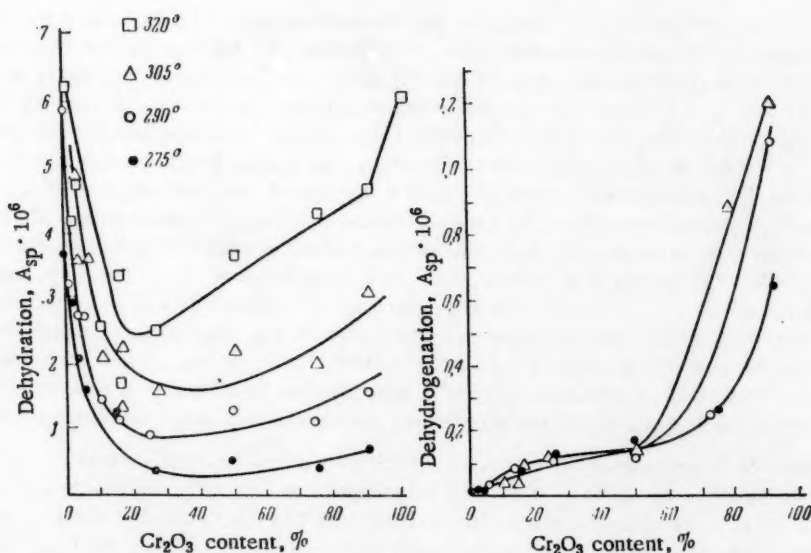


Fig. 4. Variation in specific activity of Al-Cr - 600° catalysts with composition.

It is interesting to note that the two different samples of catalysts with 3 mole %  $\text{Cr}_2\text{O}_3$  with differing activity (evaluated on the basis of degree of conversion) and nonidentical magnitude of specific surface are very close to each

other in specific activity, but the two different samples with 15%  $\text{Cr}_2\text{O}_3$  having similar activities based on degree of conversion, differ in specific activity by a factor of almost two. Here there is clearly an effect of the competitive effects of pH of precipitation (see Table 1) and a concentration factor (mutual protection of the components against crystallization) on the texture of the catalysts. This can be illustrated by the following data (Table 5).

TABLE 5. Specific Surface (S), Specific Volume (V), and Average Pore Radius ( $r_{av}$ ) of Catalysts with 3 and 15%  $\text{Cr}_2\text{O}_3$

$\text{Cr}_2\text{O}_3$ , %	pH of precipitation	$S, \text{m}^2/\text{g}$		$V, \text{cm}^3/\text{g}$		$r_{av}, \text{\AA}$	
		450°	600°	450°	600°	450°	600°
3 (I)	6,4	217	221	0,20	0,22	24	20
3 (II)	7,6	260	256	0,20	0,21	22	17
15 (I)	7,5	298	255	0,33	0,31	22	24
15 (II)	6,7	284	320	0,21	0,23	15	14

TABLE 6. Change in  $k_s$  with Catalyst Composition and Temperature of Alcohol Decomposition

$\text{Cr}_2\text{O}_3$ , mole %	450° series				600° series			
	275°	290°	305°	320°	275°	290°	305°	320°
1	0	0	0	—	1	0	0	0
3 <sub>II</sub>	0	0	0	—	1	0,4	0	0
5	2	1	0	—	1	1	0	0
10	7	3	0	—	—	2	1	1
15 <sub>I</sub>	—	—	—	—	6	5	2	2
15 <sub>II</sub>	13	12	7	—	—	8	6	4
25	15	8	7	—	25	12	8	7
50	40	20	11	—	23	9	6	3
75	50	32	32	—	39	17	30	20
90	—	50	38	—	46	41	27	35
100	—	—	—	32	—	—	—	68

In the case of the catalysts with 3%  $\text{Cr}_2\text{O}_3$  the protective effect against crystallization in the hydroxide stage is very strongly expressed; In spite of somewhat different magnitudes of S for these preparations, heating them to 600° does not give rise to a change in the magnitude of specific surface, i.e., neither of them sinter in this interval of temperatures; they both have identical specific pore volumes, also unchanged on transition from 450 to 600° calcination temperature. The average pore radii also differ little. Thus, the change in pH of precipitation has practically no effect on the texture of the catalysts with 3%  $\text{Cr}_2\text{O}_3$ , this texture having been determined mainly by the ratio of components. The catalysts with 15%  $\text{Cr}_2\text{O}_3$  show a different picture. Heating to 600° leads to a marked change in S: For 15<sub>I</sub> sintering taken place, but for 15<sub>II</sub>, on the contrary, an increase in specific surface is observed, apparently on account of an increase in its microroughness as a result of additional dehydration by the heating (in comparison with 450°). The specific pore volume of 15<sub>I</sub> is 1.5 times that of 15<sub>II</sub>. The magnitudes of average pore radii are also in this same ratio. Thus, catalyst 15<sub>II</sub>, which was precipitated in a more acidic medium, is the more fine-pored, which also explains its lower activity in comparison with 15<sub>I</sub>, since part of the pores in 15<sub>II</sub> prove to be inaccessible for the reaction. From what has been said it follows that in the case of the catalyst with 15%  $\text{Cr}_2\text{O}_3$  the decisive factor in the formation of texture was the pH of precipitation, and the mutual protection of the components against crystallization was of considerably less significance than in the case of the catalysts with 3%  $\text{Cr}_2\text{O}_3$ .

Table 6 shows the magnitudes of the selectivity coefficients of the catalysts, calculated from the specific activities by the formula  $k_s = A_{sp}H_2/\Sigma A_{sp} \cdot 100$ . The magnitude of  $k_s$  increases rapidly with an increase in the catalysts' chromic oxide content; however, even the catalysts with 90%  $\text{Cr}_2\text{O}_3$  are characterized by  $k_s \leq 50$ , and hence in the temperature range investigated they represent preferentially dehydrating catalysts, in this also differing fundamentally from the catalysts described in [9]. Examining Table 6, it may be noted also that the magnitude of  $k$  at a given  $\text{Cr}_2\text{O}_3$  content decreases with an increase in reaction temperature. This shows that within the temperature range investigated the dehydration is intensified to a greater degree than the dehydrogenation on increasing the temperature.



## SUMMARY

1. A study has been made of the influence of composition and calcination temperature of alumina-chromium catalysts on their specific activity in the dehydrogenation and dehydration of absolute isopropanol. It has been shown that the specific activity in dehydration passes through a minimum, strongly extended for the catalysts calcined at 450° and localized in the region of 15-25 mole %  $\text{Cr}_2\text{O}_3$  for the series of catalysts calcined at 600°. The specific activity in dehydrogenation increases evenly with an increase in the catalysts' chromic oxide content. The behavior of the catalysts is explained on the basis of data relating to their phase composition.

2. Alumina-chromium catalysts at 245-320° are preferentially dehydration catalysts.

3. For certain instances of the preparation of catalysts with identical  $\text{Cr}_2\text{O}_3$  content but with differing pH of precipitation there has been demonstrated a competition of a concentration factor with the conditions of precipitation in the formation of the texture of the catalysts: With predominance of the influence of the first factor (mutual protection against crystallization) more thermostable catalysts are obtained.

## LITERATURE CITED

1. A. M. Rubinshtein, A. A. Slinkin, and N. A. Pribytkova, *Izv. AN SSSR, Otd. Khim. Nauk* **1958**, 814.
2. A. M. Rubinshtein and N. A. Pribytkova, *Izv. AN SSSR, Otd. Khim. Nauk* **1960**, 173.
3. A. M. Rubinshtein, V. M. Akimov, and L. D. Kretalova, *Izv. AN SSSR, Otd. Khim. Nauk* **1958**, 929; A. M. Rubinshtein and A. A. Slinkin, *Izv. AN SSSR, Otd. Khim. Nauk* **1958**, 1054; A. M. Rubinshtein, Yu. A. El'tekov, and K. I. Slovetskaya, *Zh. fiz. khimii* **33**, 310 (1959).
4. A. M. Rubinshtein, V. M. Akimov, and A. A. Slinkin, *Izv. AN SSSR, Otd. Khim. Nauk* **1960**, 163.
5. G. Natta, R. Rigamonti, in book G. M. Schwab, *Handbuch der Katalyse*, Bd. V, Wien, Springer, 1957, p. 528.
6. G. D. Lyubarskii, *Uspekhi khimii* **27**, 316 (1958).
7. R. G. Davis, R. H. Griffith, and J. D. F. March, *Advances in catalysis* **9**, New York, 1957, p. 154.
8. A. M. Rubinshtein, A. L. Klyachko-Gurvich, and V. M. Akimov, *Izv. AN SSSR, Otd. Khim. Nauk* **1961**, 780.
9. A. M. Rubinshtein, N. A. Pribytkova, V. A. Afanas'ev, and A. A. Slinkin, *Kinetika i kataliz*, No. 1, 129 (1960).
10. A. A. Balandin and A. Kh. Bork, *Z. phys. Chem.* **B33**, 54, 73 (1936).
11. A. A. Tolstopyatova, A. A. Balandin, and E. I. Karpeiskaya, *Izv. AN SSSR, Otd. Khim. Nauk* **1958**, 1184.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

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# RATE CONSTANT AND MECHANISM OF THE REACTION OF ATOMIC OXYGEN WITH ACETALDEHYDE

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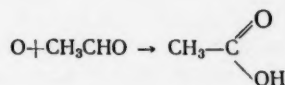
Only a few papers [1-3] have been concerned with the study of the mechanism of the interaction of atomic oxygen with acetaldehyde. In our previous paper [1] both electrical discharge in water vapor and discharge in molecular oxygen were employed for generating atomic oxygen. Experiments were carried out under jet conditions at a temperature of 100° and a pressure of 4.2 mm of Hg. In the previous paper [1] main attention was paid specifically to analysis of the reaction products. Formaldehyde, acetic acid, CO and CO<sub>2</sub> were detected as the reaction products. Experiments were carried out so that a flame was not present. On the basis of the results which we obtained from investigating the reactions of atomic oxygen both with acetaldehyde and with hydrocarbons we formulated conclusions concerning the primary reactions in the interaction of atomic oxygen with acetaldehyde. We came to the conclusion that during interaction of atomic oxygen with acetaldehyde in a jet at a comparatively low pressure (4 mm) the principal reactions were: a reaction by which an oxygen atom was introduced into the C-H bond, resulting in formation of acetic acid, and reactions occurring through cleavage of the C-C bond and resulting in formation of formaldehyde, CO and CO<sub>2</sub>. Cvetanovic [2] who studied the reaction of atomic oxygen with molecular acetaldehyde under the conditions of a photochemical method, at pressures ~100 mm of mercury, and with mercury sensitization, arrived at a different conclusion, namely that in the reaction of atomic oxygen with acetaldehyde, hydroxyl and CH<sub>3</sub>CO radicals were principally formed. Further the hydroxyl with molecular acetaldehyde gave water and the acetyl resulted in formation of diacetyl. The principal reaction products in Cvetanovic's experiments were water and diacetyl. Atomic oxygen was prepared by mercury photosensitized decomposition of N<sub>2</sub>O. Ford and Endow [3], also using a photochemical method, prepared atomic oxygen but this time from NO<sub>2</sub>, and measured the rate constant of the reaction of atomic oxygen with cis-pentene-2 at room temperature and atmospheric pressure. Using Cvetanovic's results [4] these authors calculated the absolute value of the rate constant for the reaction of atomic oxygen with acetaldehyde at room temperature and atmospheric pressure. It may be noted that in the case of the photochemical method not only the nitrogen oxides N<sub>2</sub>O and NO<sub>2</sub> but also the second component of the starting substances, as well as the reaction products are subjected to the action of the mercury sensitization, and consequently under these conditions it is more difficult to determine the primary act of the reaction than under our experimental conditions, and the easier it is to make incorrect conclusions with respect to both the reaction products and the absolute value of the rate constant.

In all our experiments on the reactions of atomic oxygen, formation of formaldehyde was a characteristic and obvious feature (in reactions of atomic oxygen with CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>3</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>2</sub>O). In Cvetanovic's experiments formaldehyde was not found. An analysis of this question, especially in connection with our recent work, where we detected surface reactions of atoms with molecules [5, 6] (for example,  $H + O_2 \xrightarrow{\text{surface}} OH + O$  and  $H + C_2H_4 \xrightarrow{\text{surface}} C_2H_5$ ), brought us to the conclusion that possibly under our experimental conditions some reaction of atomic oxygen with molecules may occur on the surface of the reaction vessel. In fact experiments conducted in which the surface had been treated differently (KCl, ZnOCR<sub>2</sub>O<sub>3</sub>) showed that the composition of the reaction products can change.

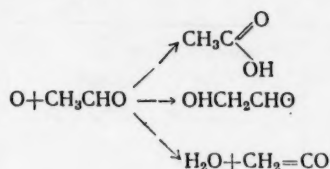
We have attempted both in this work and in previous studies to show which reactions of atomic oxygen with molecules takes place in the reaction space and which on the surface and to study the reaction kinetics under those conditions in which either the space reaction or the surface reaction predominates.

## EXPERIMENTAL

Experiments for studying the reaction of atomic oxygen with acetaldehyde were conducted in the apparatus described earlier [7]. Atomic oxygen was generated in the high voltage zone of an electrical discharge in molecular oxygen. Molecular oxygen was prepared by heating  $\text{KMnO}_4$ , during which every precaution was observed to prevent particles of  $\text{KMnO}_4$  and  $\text{MnO}_2$  entering the region of the discharge. By means of a manometer and valve cocks it was possible to maintain the pressure in the reaction vessel with an accuracy of 0.1 mm of mercury. Atomic oxygen together with undissociated molecular  $\text{O}_2$  were carried by the jet stream through the nozzle into the reaction vessel. Acetaldehyde was fed into the reaction vessel from a calibrated flask. The acetaldehyde was fed into the reaction vessel through special inlets at different distances from the nozzle. The reaction products were condensed in a detachable trap cooled with liquid nitrogen. The temperature during the reaction was measured in different parts of the reaction vessel by copper-constantan thermocouples. The vessel was heated by means of two heaters. The heaters were chosen so that the temperature was the same for the whole extent of the reaction zone. The walls of the reaction vessel were coated with KCl. Earlier [5, 6] we have shown that on "clean" surfaces or surfaces treated with phosphoric acid, surface reactions may take place. Treatment of the surface with KCl solution and also with the reaction products (a polymer was precipitated on the walls of the vessel) led to cessation of surface processes and predominantly space reactions occurred. The principal reaction products of atomic oxygen with acetaldehyde in a vessel the walls of which were KCl coated, were found to be acetic acid, ketene and glycollic aldehyde. Comparison of the maximum yield of acetic acid with the quantity of atomic oxygen entering the reaction vessel at  $130^\circ$  showed that up to 60% of the latter was used in formation of the acid. The remaining atomic oxygen (approximately 40%) was used in formation of glycollic aldehyde and ketene. Glycollic aldehyde at temperatures of  $100^\circ$  and above precipitated on the walls of the vessel as a polymer. Ketene together with acetaldehyde volatilized into the trap and could be distilled off at  $-100^\circ$ . With reduction of the reaction temperature to room temperature, 60% of the atomic oxygen was used in ketene formation and the remaining 40% in forming the acid and glycollic aldehyde. The concentration of oxygen atoms in the inlet into the reaction vessel was measured by the method described previously [8]. Formation of acetic acid is possible by two routes: either by introduction of oxygen atoms into the acetaldehyde molecule across the C-H bond or from an acetyl radical as a result of disproportionation and formation of ketene with subsequent formation of the acid on dissolving the ketene in water. A search for acetyl radicals by detection of acetyl peroxide led to a negative result. No peroxides were detected in the reaction products. The absence of any sign of the presence of acetyl radical compelled the conclusion that only one route for formation of the acid was realized - by introduction of oxygen atoms into the acetaldehyde molecule across the C-H bond



Thus it was found that interaction of atomic oxygen with acetaldehyde occurred by three routes:



At room temperature formation of ketene and water predominated, and with increase in the temperature to  $100^\circ$  and above introduction processes predominated with formation of acetic acid and glycollic aldehyde. Earlier we developed a method [7] for the measurement of the rate constants of the elementary reaction of atomic oxygen with different molecules. According to this method, in order to determine the rate constant of the reaction of atomic oxygen with any molecule it was necessary to measure the dependence of the final concentration of one of the primary products on the initial concentration of the starting product. Measurements must extend over that range of initial concentrations of the starting substance where the final concentrations of the primary product are close to the maxima i.e., the concentration limits. Then  $1/(\text{B}'_F)$  ( $\text{B}'_F$  is the final concentration of the given primary product) against  $1/\text{A}_0$  ( $\text{A}_0$  is the initial concentration of the original substance) was plotted graphically. This was a straight line, corresponding (for a bimolecular reaction) to the equation

$$1/(\text{B}'_F) = \frac{k_1}{k'_1(\text{O})_0} + \frac{[k_0 + k''_0(\text{O})_0 M]}{k_1(\text{O})_0} \cdot \frac{k_1}{k'_1(\text{A}_0)}$$

where  $k_1$  is the total rate constant of the reaction of atomic oxygen with molecules;  $k_1'$  is the rate constant of the reaction of atomic oxygen with molecules, resulting in formation of the given primary product;  $k_0$  is the rate constant of linear destruction of atomic oxygen;  $k_0''$  is the rate constant of quadratic destruction of atomic oxygen;  $(O)_0$  is the initial concentration of atomic oxygen;  $M$  is the concentration of third particles.

In this equation the quantity  $k/k_1'(O)_0$  is the intercept made by the straight line on the ordinate axis. The tangent of the angle of slope has the value:

$$\frac{[k_0 + k_0''(O)_0 M]}{k_1(O)_0} \cdot \frac{k_1}{k_1'} = \operatorname{tg} \alpha,$$

where  $k_1/k_1'(O)_0 = b$  is the known value of the intercept made on the ordinate axis;  $k_1$  is the required constant and  $k_0 + k_0''(O)_0 M$  is the total destruction of atomic oxygen. Hence the required value  $k_1$  can be calculated from the formula:

$$k_1 = \frac{[k_0 + k_0''(O)_0 M] \cdot b}{\operatorname{tg} \alpha} \quad (1)$$

providing the total destruction of atoms is known. The total destruction of atoms was determined by the method described previously [9]. According to this method, in order to determine the total destruction it is necessary to measure the relative concentration of the atoms  $(O)_0/(O)_x$  in different parts of the reaction vessel.

In our paper [9] it was shown that if the dependence of  $\log (O)_0/(O)_x$  on  $x$  was obtained as a straight line passing through the origin of the coordinates, then in this case linear destruction of atoms predominates, i.e.,  $k_0 \gg k_0''(O)_0 M$ . Usually for the destruction of atomic oxygen under our conditions we find this to be true. The constant  $k_0$  was calculated from the tangent of the angle of slope of the straight line from the formula:

$$k_0 = 2,3 \cdot w \cdot \operatorname{tg} \gamma,$$

where  $w$  is the linear rate of the jet stream;  $\gamma$  is the angle of slope of the straight line

$$\lg \frac{(O)_0}{(O)_x} = A \cdot x$$

In the present work in order to determine the relative concentration of atomic oxygen at different distances from the nozzle, we utilized the values of the limiting concentrations of acetic acid. Acetaldehyde was fed into the reaction vessel at different distances from the nozzle in such concentrations as to produce the limiting yield of acid. The ratios of the limiting yields of acid represented the ratios of the atomic oxygen concentrations.

Number of Experiment	Temperature, °C	Pressure, mm of Hg	Rate of Jet Stream cm. sec <sup>-1</sup>	Destruction Constant $k_0$ , sec <sup>-1</sup>	Reaction rate constant $k_1$ , 10 <sup>14</sup> cm <sup>3</sup> ·sec <sup>-1</sup>
1	70	3,1	243	48,3	1,1
2	80	3,1	250	57,7	1,23
3	100	3,1	260	45,0	1,78
4	120	3,1	266	61,0	1,9
5	155	3,1	340	81	2,35
6	100	1,2	160	23	1,92

In Fig. 1 is given the plot of  $\log (O)_0/(O)_x$  against  $x$  at 150° and 3.1 mm of Hg pressure. Since this a straight line then linear destruction predominates. The destruction constant calculated from the graph is equal to 81 sec<sup>-1</sup>. In Fig. 2 is given the plot of  $1/(\text{CH}_3 \cdot \text{COOH})_F$  against  $1/(\text{CH}_3 \cdot \text{CHO})_0$  at 155° and 3.1 mm of Hg pressure. The reaction rate constant calculated from this graph by means of formula (1) is equal to  $2,35 \cdot 10^{-14}$  cm<sup>3</sup>·sec<sup>-1</sup>. In an analogous way the rate constants were determined for the reaction of atomic oxygen with acetaldehyde at various temperatures at a pressure of 3.1 mm of Hg. In addition the reaction rate constant was measured at 1.2 mm of Hg pressure. The results of such measurements are presented in the table.



In Fig. 3 the values of  $\log k_1$  are plotted against  $1/T$ . The activation energy of the reaction  $O + CH_3 \cdot CHO$ , calculated from this graph is equal to  $2750 \pm 500$  cal. Thus the measured rate constant of the reaction  $O + CH_3 \cdot CHO$  can be represented as

$$k_1 = 6 \cdot 10^{-13} e^{\frac{-2750}{RT}} \text{ molecule}^{-1} \cdot \text{cm}^3 \cdot \text{sec}^{-1}$$

The value of the rate constant obtained did not agree with the value cited by Ford and Endow [3] and is approximately two orders less. However we note that the rate constant obtained by these authors for the reaction of atomic oxygen with ethylene is also nearly twice as great as the constant obtained for ethylene by other authors [10]. The reaction of formation of acetic acid (and also glycollic aldehyde) from an oxygen atom and an aldehyde molecule must be accompanied by liberation of a large amount of heat. Therefore in considering this elementary act the question arises of the effect of third particles on the reaction in the same way as in considering the case of the reaction  $O + CO \rightarrow CO_2$  [9, 11]. In a general form the effect of third particles on the addition reaction of atoms and radicals to molecules was considered in our previous paper [12] taking as example the reaction

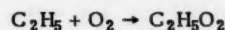


Fig. 1. Relationship between the relative concentration of atomic oxygen and the distance between the site of mixing of acetaldehyde with atomic oxygen and the position of entry of the atoms into the reaction vessel at 428°K.

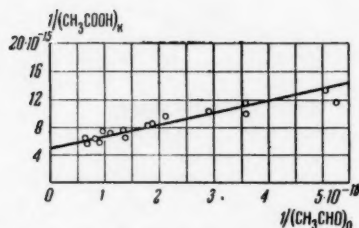


Fig. 2. Relationship between the final concentration of acetic acid and the initial concentration of acetaldehyde at a reaction temperature of 428°K.

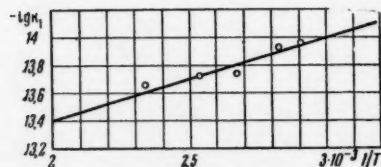
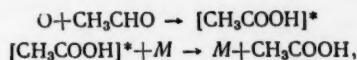


Fig. 3. Relationship between temperature and rate constant of the reaction of atomic oxygen with acetaldehyde.

have carried out experiments both with the reaction rate dependent on temperature and with it dependent on pressure, since the dependence on pressure can be more complex [12] than that considered above.

For the  $O + CH_3 \cdot CHO$  reaction we have carried out experiments at the lower pressure of  $\sim 1.2$  mm of Hg with the object of elucidating the pressure effect of third particles. The constant obtained (cf. experiment No. 6 in Table 1) indicated that in the given pressure range the reaction rate was independent of the pressure. Possibly the life-time of the excited  $[C_2H_4OO]^*$  particle is so long that already at pressures of the order of 1 mm of Hg the reaction is independent of the pressure. However possibly as in the case mentioned in paper [11] the reaction proceeds by a bimolecular mechanism. Then stabilization of the excited particle apparently occurs by emission of light. Generally speaking it can be anticipated that at the pressures with which we worked and established the temperature course of the reaction the effect of pressure cannot count. This conclusion is based on the following fact. If we imagine that the reaction of formation of acid proceeds in two stages



then the determining stage will be either the first or the second. There will be a pressure dependence in the case when the lifetime of the excited particle is small and the determining stage will be the second. It can be said in advance that the second reaction — a stabilization reaction — will take place without activation energy. The first reaction — the formation of the excited complex — is a bimolecular process and can take place with or without activation energy — this depending on the properties of the colliding particles. Consequently when we observe the activation energy of a similar type reaction then it may be assumed that the determining reaction under the present conditions is the first stage and pressure dependence will not be observed. If stabilization of the complex occurs by emission of light then likewise there will be no pressure dependence. However in all our investigations, in spite of similar considerations, we

## SUMMARY

1. The reaction of atomic oxygen with acetaldehyde was studied under conditions in which the principal reaction products were addition products—acetic acid and glycollic aldehyde.

2. The activation energy and the absolute value of the rate constant for the reaction of atomic oxygen with acetaldehyde were measured.

3. In the pressure range 1-3 mm of Hg the rate constant of the reaction of atomic oxygen with acetaldehyde was that of a constant bimolecular process.

## LITERATURE CITED

1. L. I. Avramenko and R. V. Lorentso, *Zh. fiz. khimii* **26**, 1084 (1952).
2. R. J. Cvetanovic, *Canad. J. Chem.* **34**, 775 (1956).
3. H. W. Ford and A. Noborn Endow, *J. Chem. Phys.* **27**, 1277 (1957).
4. R. J. Cvetanovic, *J. Chem. Phys.* **30**, 19 (1959).
5. L. I. Avramenko and R. V. Kolesnikova, *Zh. fiz. khimii* **32**, 2780 (1958).
6. L. I. Avramenko and R. V. Kolesnikova, *Izv. AN SSSR, Otd. Khim. Nauk* **1959**, 746.
7. L. I. Avramenko, R. V. Kolesnikova, and L. M. Postnikov, *Izv. AN SSSR, Otd. Khim. Nauk* **1958**, 277.
8. L. I. Avramenko and R. V. Kolesnikova, *Zh. fiz. khimii* **29**, 539 (1955).
9. L. I. Avramenko and R. V. Kolesnikova, *Izv. AN SSSR, Otd. Khim. Nauk* **1959**, 1562.
10. M. Lelickoff, F. F. Marmo, I. Pressman, E. R. Manring, L. M. Aschenbrand, and A. S. Jursa, *J. Geophys. Res.* **63**, 31 (1958).
11. L. I. Avramenko and R. V. Kolesnikova, *Izv. AN SSSR, Otd. Khim. Nauk* **1960**, 561.
12. L. I. Avramenko and R. V. Kolesnikova, *Izv. AN SSSR, Otd. Khim. Nauk* **1960**, 989.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. Some or all of this periodical literature may well be available in English translation. A complete list of the cover-to-cover English translations appears at the back of this issue.

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## THE SPECTRA AND STRUCTURE OF VINYL ETHERS

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The study of the influence of various functional groups on the properties of vinyl compounds and on the condition of the double bond  $C=C$  has great interest. On the one hand, the vinyl compounds have great practical significance, and on the other, the physical constants of comparatively simple molecules of the type  $C=C-X$  submit more easily to interpretation and can serve as valuable material for the study of the appearance and nature of the mutual influence of the atoms of organic compounds. In the vinyl ethers the influence of the alkoxy group on the double bond is apparent in the chemical properties — in the increased reactivity in reactions of addition, hydrolysis, etc., and in the processes of polymerization and copolymerization; the structure of the alkoxy radical is of great importance in producing these effects. There is little known about the influence of the alkoxy group on the strength of the  $C=C$  double bond and on its optical properties.

### EXPERIMENTAL

The spectra of a series of vinyl ethers containing paraffinic, naphthenic, and aromatic radicals are investigated in this work. The spectra of some of these were studied earlier [1, 2].

**Measurement technique.** The combination dispersion spectra (Raman Spectra) were photographed for the measurements of the frequency in a 3-prism spectrograph ISP-67. The 4358 Å mercury line was used for excitation. For the determination of the intensity of the lines, solutions of the vinyl ethers in  $CCl_4$  were used with a ratio of 2 M of the substance to 1 M of the solvent. The unit of intensity was taken as 1/100 of the integrated intensity of the line at  $313\text{ cm}^{-1}$  of  $CCl_4$  based on 1 M. A photoelectric spectrophotometer was used. The sensitivity was approximately  $\pm 15\%$  (numbers with the approximation sign were obtained by oriented visual estimation).

The absorption spectra were measured with photoelectric spectrophotometers SF-4 and SP-41; the latter included a vacuum double monochromator with a LiF prism. The solvent was heptane. The measurements were carried out in cooperation with V. A. Petukhov. For the two vinyl phenyl ethers in the table,  $\lambda$  and  $\epsilon$  are given only for the near absorption band; this band has a fine structure. The absorption spectra of the two hydrocarbons are taken from the literature.

The results of the measurements. In the table are given the frequency ( $\omega$  in  $\text{cm}^{-1}$ ) of the valence vibration of the double bond  $C=C$  and the intensity coefficient (I) of the corresponding line in the Raman spectra, also the wavelength ( $\lambda$  in Å) and the molar (decimal) absorption coefficient ( $\epsilon$ ) of the band maxima in the ultraviolet absorption spectra in the region 1700-4000 Å;  $f$  is the oscillator strength. The absorption curves are given in Fig. 1. The abbreviations: Et — ethyl, Pr — propyl, Bu — butyl are used in the table.

### Discussion of the Experimental Results

The majority of the vinyl ethers have several lines in the frequency region of the double bond stretching vibration which are easily observed both in the Raman spectra and in the infrared spectra; the ratios of the intensities of the components in both kinds of spectra are rather similar. The data cited in the table show that the character of the splitting of  $\omega_{C=C}$  depends only slightly on the length of the n-alkyl radicals but strongly depends on the presence of branching and rings, and on the presence or absence of  $\alpha$ -substituents.

The establishment of the causes of the splitting of the  $C=C$  line and a correlation of the individual components was important since otherwise it would be impossible to judge from the spectra the influence of the alkoxy

groups on the character of the double bond and the geometric configuration of the molecules. The geometric configuration of the molecules of the vinyl ethers is significant not only for the physical but also for the chemical properties. The influence of the configuration on the chemical properties can be correlated with both the degree of screening of the reactive center and with the variations of the conditions of the individual chemical bonds.

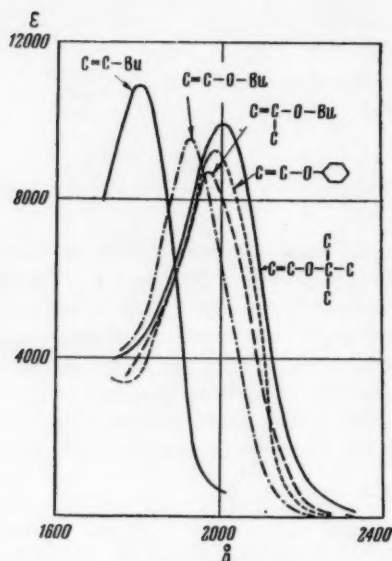


Fig. 1. The ultraviolet absorption spectra of octene-1 and of the vinyl ethers (in heptane solutions): Bu - is the butyl group,

⬡ is the cyclohexyl group.

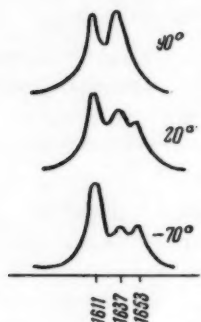


Fig. 2. Influence of the temperature on the structure of the C=C bond of vinyl butyl ether.

One of the authors of this paper in an earlier work [1] explained the splitting of the C=C band of the n-alkyl vinyl ethers into three components as due to the presence of rotational isomerization and Fermi resonance; the lines at approximately 1610 and approximately 1637  $\text{cm}^{-1}$  were related to two rotational isomers. Mikawa [2], taking into consideration that there is only one conformation (S-trans), ascribed the appearance of these two lines to Fermi-resonance. The suggested rotational isomerization could be examined by drawing on the data of the presence of splitting in other frequency regions, on data of the influence of temperature on the relative intensities of the components, on the dependence between the structure of the molecule and the spectrum in connection with the presence or absence of substituents which make more difficult the formation of the several possible conformations, and on the influence of isotopic substituents.

The influence of solvents and of the temperature on the structure of the C=C band was investigated in this work. Vinyl butyl ether was taken as an example, and it was shown that different solvents caused almost no change of the frequencies of the components, but lead to a redistribution of the intensities. If in the pure liquid and in heptane and carbon tetrachloride solutions the coefficients of the intensities of the lines at 1610 and 1637  $\text{cm}^{-1}$  are related as 1:1. This, at least, does not contradict the suggestion of the presence of rotational isomerization. The influence of the temperature could be more indicative. Experiment showed that an increase of the temperature to 90° caused the lines of vinyl butyl ether at 1610 and 1637  $\text{cm}^{-1}$  to become almost equal in intensity (Fig. 2), while at -70° the relative intensity of the line at 1637  $\text{cm}^{-1}$  is significantly lowered. Apparently the lines at 1610 and 1637  $\text{cm}^{-1}$  can be related to two different rotational isomers; the origin of the line at 1653 is not yet clear since it is difficult to establish whether its intensity is changed by increasing the temperature or whether it is incorporated into the neighboring lines.

The question arises: to which of the isomers do the lines at 1610 and 1637  $\text{cm}^{-1}$  belong. An approximate calculation of the interatomic distances in models of the molecule showed that steric factors would allow the existence of molecules of the n-alkyl vinyl ethers with a flat S-trans-form of the skeleton  $\text{C}=\text{C}-\text{O}-\text{C}$

and a non-planar warped-form, but do not allow the possibility

of the existence of a stable planar cis-form  $\text{C}=\text{C}-\text{O}-\text{C}$ . The distances (r) between the most closely positioned atoms of hydrogen of the alkoxy and the vinyl or the  $\alpha$ -methylvinyl group of the three forms mentioned above (the planar S-trans, the nonplanar warped

and the planar S-cis) for the optimum angles of rotation of the alkyl group with its chain around the O-C<sub>alk</sub> and C-C bonds (i.e., for such angles at which r is a maximum) are as follows: vinyl ethyl ether 2.5, 3.0, and 2.0 Å; vinyl tert-butyl ether 2.45, 3.0, and 1.9 Å;  $\alpha$ -methylvinyl ethyl ether 2.0, 2.7, and 2.0 Å. Configurations for which the H...H distance is substantially smaller than 2.2 Å are improbable.



Molecular structures	Raman spectra		Ultraviolet absorption spectra		
	$\omega$	$I$	$\lambda$	$\varepsilon$	$f$
$C=C-C-C-C-C$	1642 1611 1637	38 25 12	1800	11 000	0,28
$C=C-O-Et$	1652	12	1930	9000	0,25
$C=C-O-Bu$	1611 1637 1653	25 12 12	1920	9500	0,25
$C=C-O-C \begin{smallmatrix} C \\ C \end{smallmatrix}$	1612 1636 1654	$\sim 10$ $\sim 35$ $\sim 5$	1960	9000	—
$C=C-O-C \begin{smallmatrix} C \\ C \\ C \end{smallmatrix}$	1636	$\sim 100$	2000	10 000	0,27
$C=C-O-\text{C}_6\text{H}_5$	1636	50	1990	9200	0,25
$C=C-O-\text{C}_6\text{H}_4$	1636	—	—	—	—
$C=C-O-\text{C}_6\text{H}_3$	1642	80	$\sim 2720$	—	—
$C=C-O-\text{C}_6\text{H}_2$	1647	—	—	—	—
$C=C \begin{smallmatrix} C-C-C-C \\ C \end{smallmatrix}$	1654	38	1880	9000	0,22
$C=C \begin{smallmatrix} OEt \\ C \end{smallmatrix}$	1600 1659	$\sim 15$ $\sim 40$	—	—	—
$C=C \begin{smallmatrix} OBu \\ C \end{smallmatrix}$	1598 1656	14 40	1970	8500	0,25
$C=C \begin{smallmatrix} OBu \\ Et \end{smallmatrix}$	1599 1656	$\sim 15$ $\sim 40$	—	—	—
$C=C \begin{smallmatrix} OBu \\ Pr \end{smallmatrix}$	1597 1654	$\sim 15$ $\sim 40$	—	—	—
$C=C \begin{smallmatrix} O-C_6H_5 \\ C \end{smallmatrix}$	1595 1655	—	1980	7000	0,23
$C=C \begin{smallmatrix} O-C_6H_4 \\ C \end{smallmatrix}$	1674	—	$\sim 2680$	1800	—

With an increase of the degree of branching of the alkyl radical R, the interval of possible angles of rotation ( $\theta$ ) of the group OR around the bond  $C_{vin}-O$  (that is the angle between the planes  $C=C-O$  and  $C-O-C$ )

must decrease. If one allows the existence of nonplanar forms of the n-alkyl vinyl ethers which are rather close to the S-cis form, then for the vinyl cyclohexyl and vinyl tert-butyl ethers, the only forms possible differ substantially in rotational angle  $\theta$  from the planar S-cis form.\* The existence of the planar S-trans form  $C=C-O-C$  is

\* The values of  $r$  cited above are not sufficient for a judgement of the real differences since these values are pertinent only to models with the optimum angles of rotation of the individual chains R.

possible in these cases, but under the condition of a sharp limitation of the allowable rotation angle ( $\varphi$ ) of the alkyl groups around the  $O-C_{alk}$  bond. The presence of an  $\alpha$ -substituent should make more difficult the formation of the S-trans-form; the angle of rotation should be not less than  $10^\circ$ , and for  $\alpha$ -alkylvinyl cyclohexyl ethers it should be still greater. Thus, this compound can exist only in the nonplanar form of  $C=C-O-C$ . The data for vinyl tertiary butyl ether and vinyl cyclohexyl ether in any case indicate that under the condition of a substantial limiting of the possible angles  $\theta$ , there remains only one line in the region of the  $C=C$  frequency; for the  $\alpha$ -substituted n-alkyl vinyl ethers, the splitting picture observed has a completely different appearance from that of similar ethers without an  $\alpha$ -substituent.

An estimation made from a mechanical model of the molecule shows that the trans-configuration should have a slightly higher frequency for the  $C=C$  absorption than the other possible configurations. At the same time, the trans-configuration is more suitable for conjugation\* of the OR group with the  $C=C$  group, which can lead to a decrease of the  $C=C$  frequency and a strengthening of the double bond. In connection with this, one can probably correlate the more intense line of the n-alkyl vinyl ethers ( $1610\text{ cm}^{-1}$ ) with the trans-form, and the  $1637\text{ cm}^{-1}$  line with the warped form. Such a correlation, however, leaves unclarified the origin of the line of the  $\alpha$ -derivatives at approximately  $1597\text{ cm}^{-1}$ .

In order to judge of the influence of the OR group on the character of the double bond  $C=C$  in the n-alkyl vinyl ethers, we will compare their vibrational frequencies with the  $C=C$  frequency in the alkenes. For the comparison it is expedient to use the frequencies of configurations of a single kind. The 1-alkenes have one line at approximately  $1642\text{ cm}^{-1}$ . The absence of splitting in these cases can be explained as due to the absence of a substantial interaction between the double bond  $C=C$  and the alkyl radicals, and to the lack of influence of the angle of rotation of the alkyl group on the  $C=C$  frequency and on the character of the double bond, or that there is present practically only a single rotational isomer. The rotation of the OR group around the  $C_{vinyl}-O$  bond can be accompanied by a more substantial change of the character of the  $C=C$  bond; the influence of the changes of these geometrical parameters must, as before, be small. Judging by data in the literature, 1-butene and, apparently, other 1-alkenes have the warped-configuration. The predominance of the trans-form of vinyl methyl ether and of the warped form of the 1-alkene is completely possible, since the difference of the energies of the warped- and trans-forms of butene-1 is small, approximately  $1\text{ kcal/M}$ ; this difference can be somewhat greater for the vinyl ether since the  $C-O$  distance is smaller than  $C-C$ , but on the other hand the energy of the planar forms may be lowered at the expense of the conjugation of the OR group and the  $\pi$ -bond (note that for anisole, which obviously has the planar configuration, the "conjugation energy" is approximately  $8\text{ kcal/M}$ ). If the suggestion relative to the correlation of the components of the splitting is correct, then one can say that the oxygen atom of the  $OR$  in the molecules with a nonplanar configuration lowers the frequency for the  $C=C$  vibration by approximately  $6\text{ cm}^{-1}$ , and in the planar molecules, by a considerably larger amount (approximately  $30\text{ cm}^{-1}$ ). In any case, the lowering of  $\omega_{C=C}$  is quite substantial in the dominant confirmation. Obviously, it depends basically on a decrease of the strength of the  $C=C$  bond.

There is an intense absorption band around  $1900\text{--}2000\text{ A}$  in the absorption spectra of the vinyl ethers (Fig. 1), this band is somewhat closer to the visible part of the spectrum than that of the 1-alkenes. Corresponding to this, the intensity coefficient of the Raman  $C=C$  lines of the ethers is somewhat higher than that of the 1-alkenes. In the series of compounds investigated here,  $I_{C=C}$  is greater for  $\lambda$ ; this justifies the suggestion that a corresponding level of electronic excitation provides a larger contribution to the magnitude of the intensity of the  $C=C$  line, and that by electronic excitation the equilibrium interatomic  $C=C$  distance is substantially changed.

## SUMMARY

1. The combination scattering (Raman spectra) and the absorption spectra in the vacuum ultraviolet region were investigated for a series of vinyl ethers.

2. In the frequency region of the  $C=C$  valence vibration, the majority of vinyl ethers have several lines. The character of the splitting depends on the presence of branching in the vinyl group, and on the presence of an  $\alpha$ -substituent. The influence of the temperature on the intensity of the lines at approximately  $1610$  and  $1640\text{ cm}^{-1}$  of n-vinyl butyl ether is favorable to a correlation of these lines with two rotational isomers. The influence of the  $OR$  group on  $\omega_{C=C}$  can qualitatively be characterized as the presence of a tendency toward a lowering of the frequency.

\*The influence of an inductive effect [3] is improbable.

3. The wavelength of the first absorption band and the intensity of the  $C=C$  line in the Raman spectra of the vinyl ethers are greater than those of alkenes with similar structures.

#### LITERATURE CITED

1. M. I. Natuev, E. N. Prelegaeva, and M. F. Shostakovskii, *Izv. AN SSSR, Otd. Khim. Nauk* **1947**, 123.
2. Y. Mikawa, *Bull. Chem. Soc. Japan* **29**, 110 (1956).
3. P. Chlorboli, *Ann. chimica* **45**, 1193 (1955).

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

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# THE SYNTHESIS OF ESTERS OF PHOSPHINIC ACIDS CONTAINING HETEROCYCLIC RADICALS

## COMMUNICATION 7. ESTERS OF PHOSPHINIC ACID WITH MONO- AND DI-OXIDOQUINOXALINIC RADICALS

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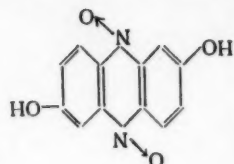
Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*,

No. 6, pp. 1016-1022, June, 1961

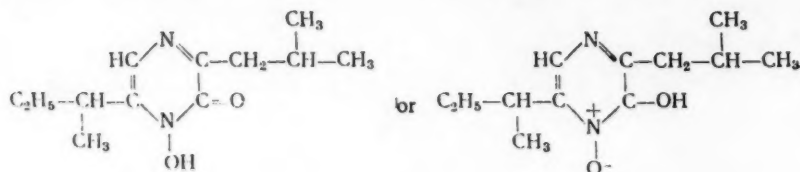
Original article submitted July 7, 1960

In recent years the attention of chemists and microbiologists has been attracted to heterocyclic compounds which contain in their composition so-called "N-oxy" groups. These N-oxy compounds have both chemical and biological interest. As has been shown by the work of contemporary English, American, Russian and Japanese investigators, similar compounds possess to various degrees physiological and antibacterial activity. Thus, in 1941 McIlwain [1] reported that iodinin, the dye of *chromobacterium iodinum*, showed considerable antibacterial activity: at a dilution of 1:1 million it is able to suppress several kinds of bacteria: *streptococcus haemolyticus*, *corynebacterium diphtheriae* etc.

The study of the chemical nature of iodinin, begun earlier by Clemo and McIlwain [2], led the authors to conclude that this antibiotic was the N,N-dioxide of 1,2-dioxyphenazine. Its formula was finally established by the Soviet chemist Kiprianov et al. [3]. The latter ascribed to iodinin the structure: N,N'-dioxide of 1,5-dioxyphenazine.

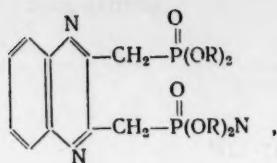


The authors were later able to synthesize iodinin itself [4]. *Aspergill*ic acid is known in medicine as a strong antibiotic, the region of action of which is much wider than that of penicillin; it appears to be a derivative of pyrazine



The N-oxides of pyridine and quinoline [5], the mono- and di-N-oxides of quinoxaline and their various derivatives [6] are also known. Several hydroxy- and methoxy-derivatives of quinoxaline studied by King, Clark and Davis [7] showed anti-bacterial activity close to that of iodinin. Our problem was to obtain and study the properties of phosphinic esters containing the N-oxy-quinoxalinic group, i.e., compounds with possible biological activity. In the present work we propose syntheses of compounds with mono-N and di-N-oxy-quinoxalinic radicals starting from the previously prepared esters

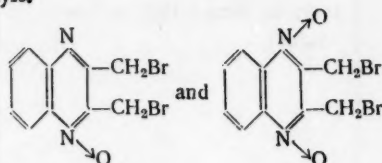




which were studied earlier by us [8].

However experiments on the oxidation of these esters under conditions described by Landquist [6] for the oxidation of quinoxaline itself and some of its derivatives did not give positive results. In this case we obtained the original ester or a mixture of unknown composition (upon longer heating). The application of more concentrated solutions of acetyl hydroperoxide (23.5 and 56.5% in glacial acetic acid), and also oxidation by hydrogen peroxide in glacial acetic acid led to partial or complete tar formation. There are indications in the literature (Newbold Spring, Elina and Magidson [9-11]) that the presence of some substituents in the ortho position to the nitrogen of the quinoxaline nucleus hinder its oxidation sterically. It is possible that in our case we have also met with a similar fact.

Esters of phosphinic acids with mono-N- and di-N-oxidoquinoxalinic radicals were obtained by us in good yield by the rearrangement reaction of A. E. Arbuzov. The mono-N- and di-N-oxides of 2,3-di-( $\omega$ -bromomethyl) quinoxaline were taken as the halogen alkyls.



The reactions of the N-oxides with phosphites were carried out in benzene or toluene at the boiling point of the solvent. The ethyl and methyl esters were easily crystallized from the reaction mixture, but the propyl with great difficulty. The allyl ester could not be separated in the crystalline state.

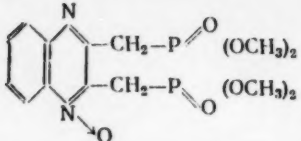
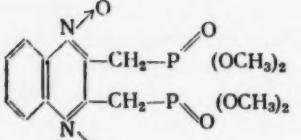
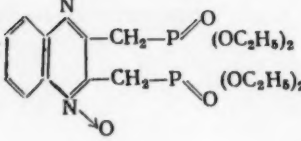
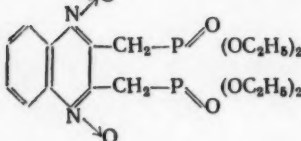
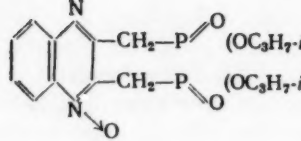
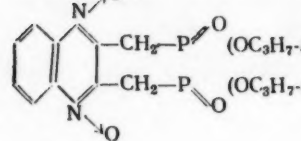
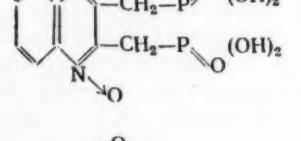
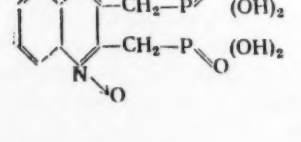
The physical properties of the esters are given in the table.

None of the esters described above are stable to light. In light they become covered with an orange film because of decomposition. The melting points of the esters with a mono-N-oxidoquinoxalinic radical are somewhat higher than the corresponding esters with an unoxidized quinoxalinic radical (an exception is the ester with the methyl radical, see [8]). The esters which contain the di-N-oxide of the quinoxalinic radical melt considerably higher. Esters of the mono-N- and di-N-oxides of 2,3-di-( $\omega$ -phosphonemethyl)quinoxaline dissolved in the ordinary organic solvents and in water, the ethyl and methyl esters being most soluble in water and the isopropyl ester considerably less soluble. The products of the hydrolysis of the esters — the phosphinic acids with N-oxidoquinoxalinic radicals — are also crystalline substances; they decompose above 200° without melting.

All of the compounds synthesized by us were given to Prof. B. L. Mazur of the Kazan State Medical Institute for testing as antibacterials.

#### EXPERIMENTAL

The interaction of the mono-N-oxide of 2,3-di-( $\omega$ -bromomethyl)-quinoxaline with trimethyl phosphite. 1.1 g of the mono-N-oxide of 2,3-di-( $\omega$ -bromomethyl)-quinoxaline and 0.82 g of trimethyl phosphite were heated in 10 ml of dry benzene under reflux on a boiling water bath for 3.5 hr. The evolution of methyl bromide was observed; when lighted it burned with a greenish flame. Toward the end of the heating the reaction mixture changed from orange to light yellow. Half of the benzene was distilled off and 2 ml of n-hexane was added to the mixture. When the walls of the flask were rubbed with glass rod, 1.2 g of a yellow precipitate appeared (95.23% of the theoretical). The latter was twice crystallized from a mixture of benzene and n-hexane (1:1); activated charcoal was used. Slightly yellowish needles were obtained with m. p. 111-112°. The product was quite soluble in ether, methyl and ethyl alcohols, and also in water. The analysis of the product was carried out by heating it in sealed tubes with concentrated nitric acid; this same procedure was used for all of the subsequent cases. Found: P 15.63, 15.47%.  $C_{14}H_{20}N_2P_2O_7$ . Calculated: P 15.89%. According to the analytical data the product was the dimethyl ester of the mono-N-oxide of 2,3-di-( $\omega$ -phosphonemethyl)quinoxaline.

Formula	Melting point	Remarks
	111-112° Melts to form a yellow liquid	Slightly yellowish needles from a mixture of benzene and n-hexane
	148-150° Melts to form a dark yellow liquid	Light yellow needles from a mixture of benzene and n-hexane
	110-112° Melts to form a light yellow liquid	Light yellow, thin needles from a mixture of benzene and n-hexane
	136-138° Melts to form a yellow liquid	Light yellow prisms from a mixture of benzene and petroleum ether
	104-105.5° Melts to form a yellow liquid	Tiny prisms from n-heptane
	127-129° Melts to form a dark yellow liquid	Yellow prisms from n-heptane
	Decomposes above 200° - does not melt	Yellow crystals from water
	At 210-212° is converted to a black tar	Yellow crystals from water

For hydrolysis, 0.5 g of the product was heated with 5 ml of dilute HCl (1:1) in a sealed tube on a boiling water bath for 5 hr. The liquid was then evaporated on a water bath until the hydrogen chloride was completely removed. The residue was dissolved in water, and the solution was boiled with activated charcoal. After the removal of the charcoal, the filtrate was again evaporated on a water bath to a small volume. Yellow crystals were deposited. They darkened on heating to 200°, and at 210-215° they were converted to a black tar. The substance was not soluble in benzene or acetone and only slightly soluble in alcohol; it was more soluble in water. Found: P 17.96%.  $C_{10}H_{12}O_7P_2N_2$ . Calculated: P 18.55%.

The interaction of the mono-N-oxide of 2,3-di-( $\omega$ -bromomethyl)-quinoxaline with triethyl phosphite. 2.4 g of the mono-N-oxide of 2,3-di-( $\omega$ -bromomethyl)-quinoxaline and 2.41 g of triethyl phosphite in 10 ml of dry toluene were heated in an oil bath. The evolution of ethyl bromide was observed at bath temperatures of 100-115°. The reaction mixture was heated for 3 hr at the temperature of the boiling solvent. On the following day, when the flask was shaken, the contents crystallized. The yield was 2.45 g (76.08% of theoretical) of the diethyl ester of the mono-N-oxide of 2,3-di-( $\omega$ -phosphonemethyl)-quinoxaline in the form of yellowish crystals, which after two crystallizations from a mixture of benzene and petroleum ether (70-100°) melted to a light yellow liquid at 110-111°. A sample mixture with the ethyl ester of 2,3-di-( $\omega$ -phosphonemethyl)-quinoxaline gave a depression: 90-97°. The substance was quite soluble in benzene, acetone, chloroform, ethyl and methyl alcohols, less soluble in ether, and quite soluble in water. P 13.60, 13.48%.  $C_{18}H_{28}O_7P_2N_2$ . Calculated: P 13.86%.

For hydrolysis, 0.5 g of the substance and 15 ml of dilute HCl (1:1) were heated in a sealed tube at 100° for 7 hr. The product of the reaction was recrystallized from water with the use of activated charcoal. The crystalline product decomposed when heated higher than 200°, and at 215-217° it changed without melting to a black mass. Found: P 18.05, 18.00%.  $C_{10}H_{12}O_7P_2N_2$ . Calculated: P 18.55%.

The interaction of the mono-N-oxide of 2,3-di-( $\omega$ -bromomethyl)-quinoxaline with triisopropyl phosphite. 1.76 g of the mono-N-oxide of 2,3-di-( $\omega$ -bromomethyl)-quinoxaline, 2.2 g of freshly distilled triisopropyl phosphite [b. p. 68.5-69.5° (15.5 mm);  $n_D^{20}$  1.4128] and 10 ml of toluene were heated under reflux at the boiling point of the toluene for 3 hr. At the conclusion of the reaction, several drops of the mixture were placed on a watch glass, several drops of n-hexane were added, and the mixture was energetically rubbed with a glass rod. Tiny crystals soon appeared; the rest of the reaction mixture was seeded with these. On the following day 0.8 g (30.07% of the theoretical) of almost colorless crystals were filtered off; after recrystallization from n-heptane these melted at 104-105.5° to a yellow liquid. A sample mixture with the isopropyl ester of 2,3-di-( $\omega$ -phosphonemethyl)-quinoxaline melted at 92-103°. Found: P 12.82%.  $C_{22}H_{36}N_2P_2O_7$ . Calculated: P 12.34%. The product thus appears to be the diisopropyl ester of the mono-N-oxide of 2,3-di-( $\omega$ -phosphonemethyl)-quinoxaline. The physical properties of the substance were similar to those of the preceding product. Its solubility in water was slightly lower than the solubility of the esters containing methyl and ethyl radicals.

The interaction of the mono-N-oxide of 2,3-di-( $\omega$ -bromomethyl)-quinoxaline with triallyl phosphite. One g of the mono-N-oxide of 2,3-di-( $\omega$ -bromomethyl)-quinoxaline, 1.2 g of triallyl phosphite, and 10 ml of benzene were heated at the boiling point for 6 hr. A dark liquid was obtained which did not crystallize when rubbed with a glass rod or addition of n-hexane or petroleum ether. After removal of the solvent, an attempt was made to distill the residue under an oil pump vacuum. But decomposition began at an oil bath temperature of 170°. A solid, black, tarry mass removed in the distillation flask. A repetition of the experiment again yielded the dark uncrystallizable liquid. The latter after removal of the solvent was subjected to hydrolysis by dilute (1:1) hydrochloric acid in a sealed tube at 100° for 6 hr. The dark liquid obtained was evaporated on a water bath for complete removal of the hydrogen chloride. The residue was boiled with water and activated charcoal, and the filtrate was concentrated to a minimum volume. The product was a noncrystalline dark tarry liquid.

The interaction of the di-N-oxide of 2,3-di-( $\omega$ -bromomethyl)-quinoxaline with trimethyl phosphite. A mixture of 2.08 g of the di-N-oxide of 2,3-di-( $\omega$ -bromomethyl)-quinoxaline, 1.48 g of freshly distilled trimethyl phosphite, and 20 ml of dry benzene were boiled under reflux for 2.5 hr (evolution of methyl bromide occurred). The orange-red liquid became yellow toward the end of the heating period. The addition of petroleum ether (70-100°) and rubbing with a glass rod caused the product to crystallize. The weight of crude product was 1.64 g (67.76% of the theoretical).

By recrystallization from a mixture of benzene and n-hexane, there were obtained tiny, light yellow needles of m. p. 148-150°. The crystals melted to a dark yellow liquid. Found: P 15.05%.  $C_{14}H_{20}N_2P_2O_8$ . Calculated: P 15.26%. The product appeared to be the dimethylester of the di-N-oxide of 2,3-di-( $\omega$ -phosphonemethyl)-quinoxaline. The substance was soluble in the majority of organic solvents and in water.

The interaction of the di-N-oxide of 2,3-di-( $\omega$ -bromomethyl)-quinoxaline with triethyl phosphite. 1.7 g of the di-N-oxide of 2,3-di-( $\omega$ -bromomethyl)-quinoxaline, 1.66 g of triethyl phosphite, and 15 ml of dry toluene were heated on an oil bath at the boiling point of the solvent for 2 hr. A dark-red liquid was obtained. Crystallization did not occur on standing overnight, but by shaking the flask it soon began. Yellow needles, 0.7 g (31.2% of the theoretical) were removed by filtration; after washing with petroleum ether they melted at 131-135°. After recrystallization from a mixture of benzene and petroleum ether the diethyl ester of the di-N-oxide of 2,3-di-( $\omega$ -phosphonemethyl)-quinoxaline was obtained in the form of light yellow crystals with m. p. 136-138°. The product was quite soluble in benzene, chloroform, and acetone, less soluble in ether, and poorly soluble in petroleum ether. It was quite soluble in water. Found: P 14.09, 14.11%.  $C_{18}H_{28}O_8P_2N_2$ . Calculated: P 13.41%.

The hydrolysis of the ester was carried out as described in the first experiment. A mixture of 0.5 g of the substance and 15 ml of dilute HCl (1:1) was heated in a sealed tube at 100° for 5 hr. The product of the hydrolysis was recrystallized from water with activated charcoal. The yellow crystals began to change when heated to approximately 200°, becoming dark colored, and at 210-212° they melted with foaming to a black liquid. Found: P 17.72%.  $C_{16}H_{12}N_2P_2O_8$ . Calculated: P 17.71%.

The interaction of the di-N-oxide of 2,3-di-( $\omega$ -bromomethyl)-quinoxaline with triisopropyl phosphite. To 1.73 g of triisopropyl phosphite dissolved in 10 ml of dry benzene was added 1.45 g of finely divided di-N-oxide of 2,3-di-( $\omega$ -bromomethyl)-quinoxaline. Immediately the liquid above the yellow dioxide became a bright rose-red color. On heating over a boiling water bath the mixture boiled; all of the solid dissolved, and the solution gradually began to take on a yellow color. The heating was continued for 3 hr. Toward the end of the heating, the solution became dark-red. After boiling 5 times with activated charcoal, it became somewhat lighter. n-Hexane was added, and the mixture was allowed to stand overnight; 0.4 g (18.52% of the theoretical) of yellow crystals precipitated. Recrystallized from a mixture of benzene and petroleum ether (40-60°), the crystals melted at 127-129° (to form a dark liquid). Found: P 11.97%.  $C_{22}H_{36}N_2P_2O_8$ . Calculated: P 11.96%. According to the analytical data the substance was the diisopropyl ester of the di-N-oxide of 2,3-di-( $\omega$ -phosphonemethyl)-quinoxaline. The substance resembled in physical properties the preceding products.

The interaction of the di-N-oxide of 2,3-di-( $\omega$ -bromomethyl)-quinoxaline with triallyl phosphite. A gram of the di-N-oxide of 2,3-di-( $\omega$ -bromomethyl)-quinoxaline and 1.75 g of freshly distilled triallyl phosphite (b. p. 87-87.5°, 8-8.5 mm) was heated under reflux in 10 ml of dry benzene for 6 hr. After removal of the benzene there remained a dark red, viscous, noncrystallizable liquid. A Beilstein test was negative. The product was soluble in acetone, ether, alcohol, and water.

An attempt to hydrolyze the liquid with dilute (1:1) hydrochloric acid by heating in a sealed tube for 6 hr at 100° did not give the desired results. A dark tarry product was obtained which could not be purified by numerous applications of activated charcoal.

#### SUMMARY

By the interaction of the mono-N- and di-N-oxides of 2,3-di-( $\omega$ -bromomethyl)-quinoxaline with trialkyl phosphites there was synthesized a series of esters of phosphinic acid containing mono-N- and di-N-oxidoquinoxalinic radicals; some of their properties were studied.

#### LITERATURE CITED

1. H. McIlwain, *Nature* **148**, 628 (1941).
2. G. R. Clemon and H. McIlwain, *J. Chem. Soc.*, **1938**, 479.
3. A. I. Kiprianov, S. B. Serebryanyi, and V. P. Chernetskii, *Doklady Akad. Nauk SSSR* **69**, 651 (1949).
4. B. S. Serebryanyi, V. P. Chernetskii, and A. I. Kiprianov, *Doklady Akad. Nauk SSSR* **70**, 645 (1950).
5. E. Ochla, *J. Organ. Chem.*, **18**, 534 (1953).
6. J. K. Landgult, *J. Chem. Soc.*, **1953**, 2816.
7. F. E. King, N. G. Clark, and P. M. H. Davis, *J. Chem. Soc.*, **1949**, 3012.
8. B. A. Arbuzov and V. M. Zoroastrova, *Izv. AN SSSR, Otd. Khim. Nauk* **1954**, 806.
9. G. T. Newbold and F. S. Spring, *J. Chem. Soc.*, **1948**, 519.
10. A. S. Elina and O. Yu. Magidson, *Zh. obshch. khimii* **25**, 161 (1955).
11. A. S. Elina, *Zh. obshch. khimii* **29**, 2763 (1959).



# ON IMIDES OF THE PHOSPHORUS ACIDS

## COMMUNICATION 7. AMIDE-IMIDE TAUTOMERISM OF THE AMIDES

### OF PENTAVALENT PHOSPHORUS ACIDS

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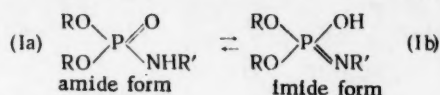
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In connection with a systematic investigation of the tautomerism of organophosphorus compounds [1], it appeared interesting to inquire into the tautomerism of the amides of pentavalent phosphorus acids, for example:



By analogy with lactim-lactam tautomerism, and that of the carboxylic acid amides in general, such tautomerism appears completely possible. However, to the present time no example of such tautomerism has been demonstrated.

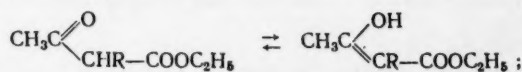
For the elucidation of this question we selected as the method of investigation the study of the influence of electrophilic substituents (in our example — those found on the nitrogen atom of the amidophosphate) on the position of the hydrogen atom in the molecule. If forms (Ia) and (Ib) are found in tautomeric relation, then the position of the tautomeric equilibrium under otherwise equal conditions will depend on the electrophilic strength of the radical R'. For a weakly electrophilic radical R', the equilibrium must be displaced practically completely in the direction of the form (Ia), since the hydroxyl-containing form (Ib) must be a considerably stronger acid than (Ia), which contains the hydrogen atom on the nitrogen; it is known that a tautomeric equilibrium is displaced in the direction of the form which appears as the weaker acid [2].

In proportion to the increase of the electrophilic strength of the radical R', for example in the series



the amide form (Ia) must become more strongly acidic at the same time as the acidity of the imide form (Ib) less sharply increases. Consequently, the equilibrium will be gradually displaced in the direction of the form (Ib), and it must be proposed that for strongly electrophilic substituents, such as PO(OR)<sub>2</sub> or SO<sub>2</sub>R, it will be completely displaced toward form (Ib).

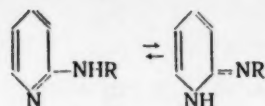
One can cite many examples of the displacement of a tautomeric equilibrium by the introduction into the molecules of the tautomeric substance of substituents with gradually increasing electrophilic strength. Thus, in the case of the alpha-substituted derivatives of acetoacetic ester,



the increasing electrophilic strength of the radical R displaces the equilibrium toward the enol form (since the acidity of the ketone form is increased by this more rapidly than the enol); this displacement is illustrated by the following data:

R	C <sub>6</sub> H <sub>5</sub>	H	C <sub>6</sub> H <sub>5</sub>	COOC <sub>2</sub> H <sub>5</sub>	COCH <sub>3</sub>
% enol	3,0 [3]	7,4 [4]	30,5 [3]	64 [5]	90 [5]

Precisely this type of phenomenon was observed and successfully used by Sheinker [6] during the investigation of tautomerism in a series of N-substituted  $\alpha$ -aminopyridines and  $\alpha$ -aminothioazoles, for example

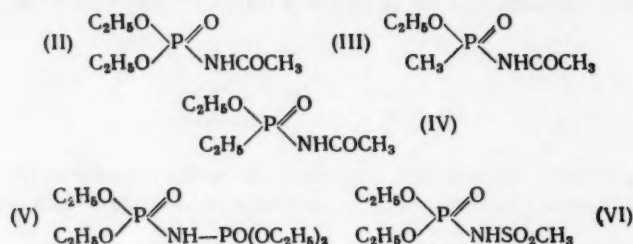


The content of the pyridonimine form increases with the change to more electrophilic substituents R of the series

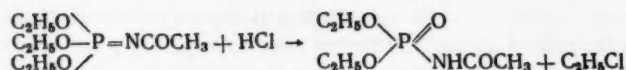


One can conclude from an examination of the data of the literature on the infrared spectra of dialkyl-N-alkyl- (or aryl)-amido phosphates [(Ia) or (Ib), R' = Alk or Aryl] that these substances have the amide structure or, that if they are tautomeric the equilibrium is displaced toward the amide form (Ia) [7].

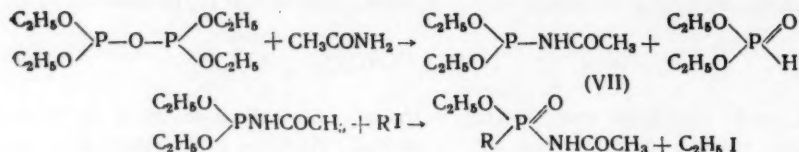
We attached electrophilic groups - acetyl, phosphoryl, and methylsulfonyl to the nitrogen atom of such substances, and obtained the following N-substituted amidophosphates and amidophosphenates



Diethyl N-acetylamidophosphate (II) was obtained by the dealkylation of triethyl N-acetylamidophosphate with dry hydrogen chloride



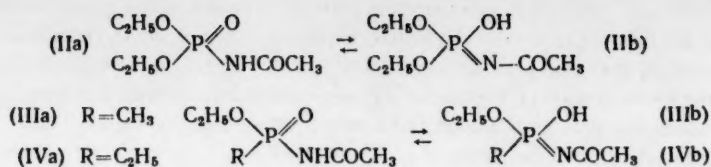
The synthesis of the O-ethyl-N-acetylamidoalkylphosphenates (III and IV) was realized according to the following scheme:



Thus by the action of acetamide on tetraethyl pyrophosphite in a manner analogous to the action of amines [8], diethyl N-acetylamidophosphite (VII) was obtained; this was then subjected to the Arbuzov rearrangement through the action of methyl and ethyl iodides. The reaction of tetraethyl pyrophosphite with acetamide occurred at room temperature in ten days. The Arbuzov rearrangement of diethyl N-acetylamidophosphite with methyl iodide occurred with the evolution of heat when it was mixed with the reagent; the rearrangement with ethyl iodide required heating for six hours at 70-80°.

The synthesis of diethyl N-diethylphosphorylamidophosphate and diethyl N-methylsulfonylamidophosphate was described by us in the preceding communication of this series [9].

The infrared spectra of these substances are given in Fig. 1. According to the data of the infrared spectra, N-acetyl substituted amidophosphates and amidophosphenates, just as N-alkyl derivatives, have the amide structure (IIa), (IIIa), (IVa), or the tautomeric equilibrium is displaced in the direction of these forms



Thus, in the spectra of diethyl N-acetylamidophosphate and O-ethyl-N-acetylamidoalkylphosphenate (see Fig. 1), there are intense absorption bands in the 1200-1250, 1700, and 3100  $\text{cm}^{-1}$  regions, which can be related respectively to the valence vibrations of  $\text{P}=\text{O}$ ,  $\text{C}=\text{O}$  and  $\text{N}-\text{H}$  [10].

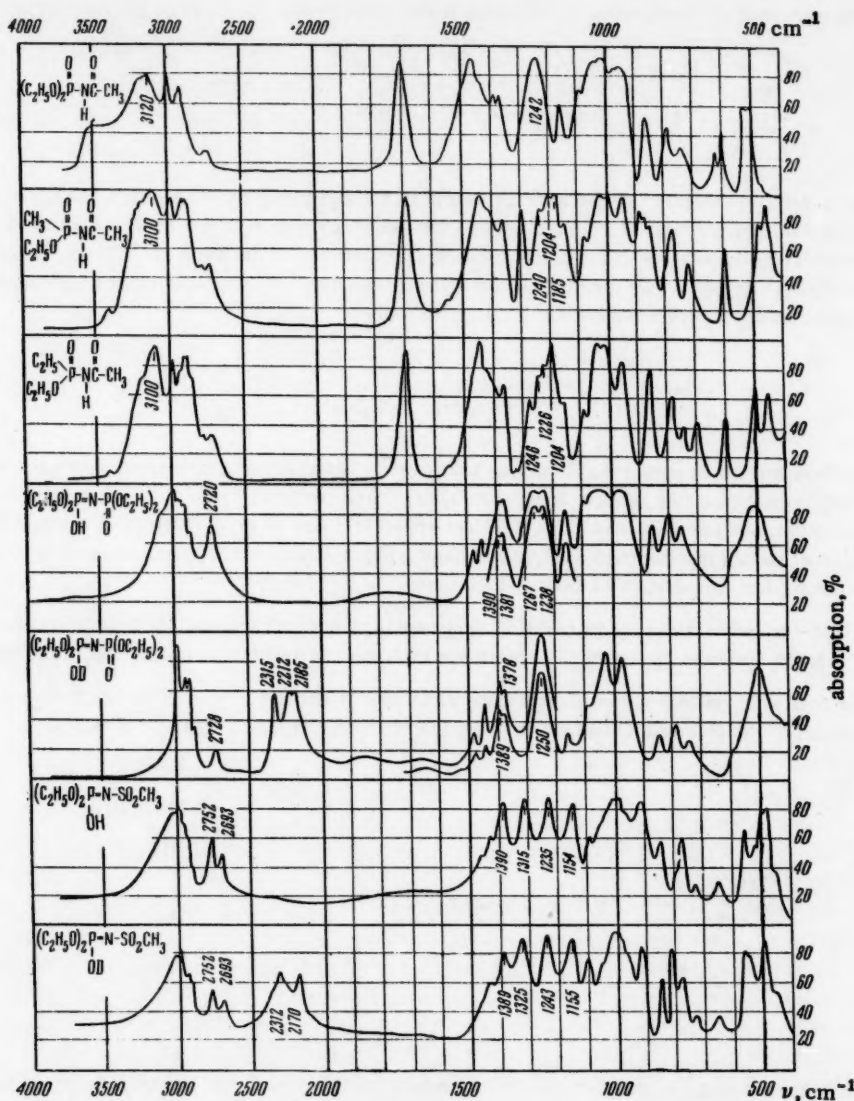
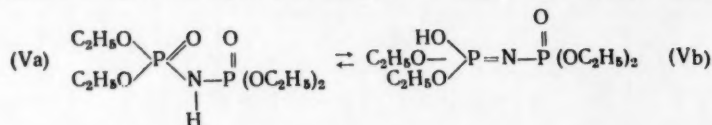


Fig. 1.

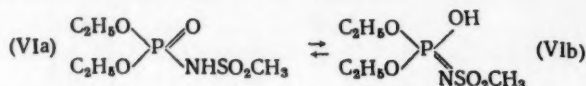
The spectra of diethyl N-diethylphosphorylamidophosphate and diethyl N-methylsulfonylamidophosphate have a different appearance. In the infrared spectrum of diethyl N-diethylphosphorylamidophosphate there is a doublet at 1238 and 1267  $\text{cm}^{-1}$  caused by the phosphoryl group  $\text{P}=\text{O}$ . Of greater interest however is the absorption band with

2 maxima at 1381 and 1390  $\text{cm}^{-1}$  which one can correlate with the presence of the group  $\text{P}=\text{N}$ . We have shown earlier in a study [11] of the infrared spectra of the imidophosphates  $(\text{RO})_3\text{P}=\text{NC}_6\text{H}_5$ ,  $(\text{RO})_3\text{P}=\text{NCOCH}_3$  and imido-phosphonates  $\text{R}'(\text{RO})_2\text{P}=\text{NC}_6\text{H}_5$  that absorption in the 1325-1385  $\text{cm}^{-1}$  region in the spectra of the imidophosphates can be correlated with the  $\text{P}=\text{N}$  group [11]. Further, in the spectra of diethyl N-diethylphosphorylamido phosphate there are observed shallow bands in the 3000  $\text{cm}^{-1}$  region and a rather intense band in the 2720  $\text{cm}^{-1}$  region which can be correlated with the valence vibration of the hydroxyl group involved in a hydrogen bond. In the spectra of solutions of these substances in carbon tetrachloride a change in the intensity of these bands is observed by dilution from 1 to 0.2 M. This is evidently due to the presence of intermolecular hydrogen bonding.

The presence of the OH and  $\text{P}=\text{N}$  bands, and the absence of a clearly expressed NH band in the infrared spectrum of diethyl N-diethylphosphorylamidophosphate allows one to conclude that this substance has the imide structure and consequently that the tautomeric equilibrium is displaced in the direction of the form (Vb).



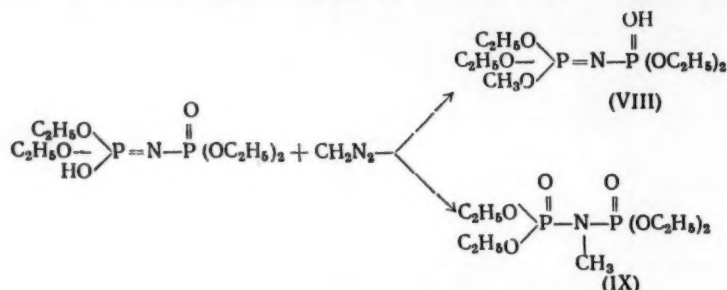
By deuterization (replacement of the hydrogen atom of the OH-group by deuterium), the spectrum of diethyl N-diethylphosphorylamidophosphate is changed only in the frequency region of the hydroxyl group: there is a decrease in the intensity of the shallow band in the 3000  $\text{cm}^{-1}$  region and of the band at 2720  $\text{cm}^{-1}$ , and new bands appear in the 2185-2315 region. The spectrum of diethyl N-methylsulfonylamidophosphate also shows the displacement of the tautomeric equilibrium toward the imide form (VIb).



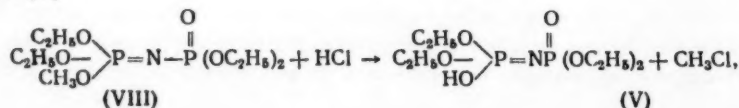
In the spectrum there are bands with a maximum at 1390  $\text{cm}^{-1}$  - a frequency characteristic of the  $\text{P}=\text{N}$  group, and the hydroxyl group frequencies (the shallow band at 3000  $\text{cm}^{-1}$  and narrower bands with maxima at 2752 and 2693  $\text{cm}^{-1}$ ). The absorption bands at 1315 and 1235  $\text{cm}^{-1}$  are apparently due to the vibrations of the sulfonyl group [10]. Monodeuterization of the diethyl N-methylsulfonylamidophosphate also causes displacement of its OH frequencies and the appearance of new frequencies at 2312 and 2170  $\text{cm}^{-1}$ .

Thus the introduction of more electrophilic substituents - phosphoryl and methylsulfonyl residues - to the nitrogen atom in the amidophosphate apparently displaces the tautomeric equilibrium toward the imide form.

Interesting data were obtained from the reaction of diethyl N-diethylphosphorylamido phosphate with diazomethane. A mixture of the isomeric O- and N-methylated products (VIII) and (IX) was obtained.



For confirmation of the presence of the O-methylated product (VIII) we made use of the reaction of such substances with dry hydrogen chloride which we described in the preceding communication [9]. By treatment of the mixture obtained above with hydrogen chloride, the O-methylated product (VIII) was reconverted to diethyl N-diethylphosphorylamidophosphate (V).

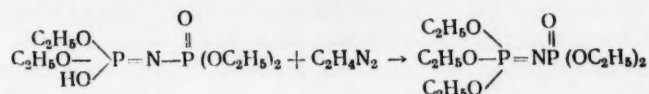




from which a salt was prepared with dibenzylamine. This salt was identical with that prepared from a known sample of diethyl N-diethylphosphorylamidophosphate (m. p. and mixed m. p. 116,5-117°).

Diethyl N-methyldiethylphosphorylamidophosphate (the product of N-methylation) was not changed by the action of hydrogen chloride, and was isolated in approximately 30% yield. Its physical constants were practically identical with the constants of the preparation described earlier by B. A. Arbuzov, et al.; thus, for the substance obtained by us b. p. 105-106° (0,3 mm);  $n_D^{20}$  1.4372,  $d_4^{20}$  1.1664. Data from the literature [12]: b. p. 138-139° (3 mm);  $n_D^{20}$  1.4353;  $d_4^{20}$  1.1666.

Diethyl N-diethylphosphorylamidophosphate with diazoethane formed only the product of O-ethylation—triethyl N-diethylphosphorylamidophosphate, the physical constants of which coincided with the constants of a known sample.



This substance was completely converted by the action of hydrogen chloride to diethyl N-diethylphosphorylamidophosphate, the dibenzylamine salt of which was identical with the dibenzylamine salt of a known sample of diethyl N-diethylphosphorylamidophosphate (m. p. and mixed m. p. 116,5-117,0°).

## EXPERIMENTAL

**Diethyl N-acetylamidophosphate (II).** Dry hydrogen chloride was passed through 1,8 g of triethyl N-acetyl-imidophosphate [11] for 15 min at 15-20°. The excess hydrogen chloride and ethyl chloride were then removed in a vacuum, and to the crystalline residue ether was twice added and removed to eliminate traces of hydrogen chloride; the weight of the residue was 1,6 g; m. p. 47-48°. The substance was purified by reprecipitation from an ether solution by the addition of petroleum ether (b. p. 30-40°). The yield of diethyl N-acetylamidophosphate was 1,1 g (70%), m. p. 49-49,5°. Found: N 7,1, 7,3%.  $\text{C}_6\text{H}_{14}\text{O}_4\text{NP}$ . Calculated: N 7,2%. The crystals were soluble in ether, chloroform, and alcohol, difficultly soluble in petroleum ether.

**Diethyl N-acetylamidophosphite (VII).** All of the syntheses and other reactions of the substances given below were carried out in an atmosphere of dry nitrogen. To 25,1 g (0,1 M) of tetraethyl pyrophosphite was added 5,2 g (0,09 M) of acetamide and the mixture was allowed to stand at room temperature. After 10 days the acetamide had reacted completely with the formation of a homogeneous solution. The diethyl phosphite formed was removed at 0,2 mm pressure and a bath temperature of 90° (the yield of diethyl phosphite was 11,2 g—90% of the theoretical;  $n_D^{20}$  1,4080). From the residue after 2 distillations there was isolated 13,9 g (78%) of diethyl N-acetylamidophosphite, m. p. 49-51° ( $1 \cdot 10^{-4}$  mm);  $n_D^{20}$  1,4600;  $d_4^{20}$  1,0854; yield 78%. Found: C 40,1, 40,5; H 7,9, 8,2; P 17,1, 17,4%. MR 45,20.  $\text{C}_6\text{H}_{14}\text{O}_3\text{NP}$ . Calculated: C 40,2; H 7,9; P 17,3%. MR 44,86.\* Diethyl N-acetylamidophosphite was a colorless liquid soluble in organic solvents.

**Ethyl N-acetylamidomethylphosphinate (II).** On the addition of 4,7 g of methyl iodide to 5,8 g of diethyl N-acetylamidophosphite (equimolar quantities) the mixture became hot and began to boil. (The flask was cooled with cold water). After three hours of reflux at 70°, followed by removal of the volatile products in a water pump vacuum, the residue was distilled. A colorless viscous liquid was obtained, 3,2 g (60,4%), b. p. 82,5-83° ( $1 \cdot 10^{-3}$  mm);  $n_D^{20}$  1,4515;  $d_4^{20}$  1,1632. The substance crystallized on standing, m. p. 42-43°. Found: C 36,1, 36,3; H 7,4, 7,5; P 18,4, 18,3%. MR 38,26.  $\text{C}_5\text{H}_{12}\text{O}_3\text{NP}$ . Calculated: C 36,4; H 7,3; P 18,8%. MR 38,05.

**Ethyl N-acetylamidoethylphosphinate (IV).** A mixture of 6,0 g of diethyl N-acetylamidophosphite and 5,2 g of ethyl iodide (equimolar quantities) was heated at 70-80° under reflux until a negative reaction was obtained for P = with phenyl azide (6 hr). The yield of ethyl N-acetylamidoethylphosphinate was 4,3 g (71,4%); b.p. 84° ( $1 \cdot 10^{-3}$  mm);  $n_D^{20}$  1,4509;  $d_4^{20}$  1,1265. Found: C 39,9, 40,2; H 7,8, 7,7; P 17,2, 17,0; N 8,4, 8,2%. MR 42,82.  $\text{C}_6\text{H}_{14}\text{O}_3\text{NP}$ . Calculated: C 40,2; H 7,9; P 17,3; N 7,9%. MR\* 42,67. The ester was a colorless liquid soluble in water, benzene, and alcohol, but not soluble in petroleum ether.

\* The AR of nitrogen was taken to be 2,42 [13].

The dibenzylamine salt of diethyl N-diethylphosphorylamidophosphate. To 0.419 g of diethyl N-diethylphosphorylamidophosphate was added 0.286 g of dibenzylamine (equimolar quantities); the mixture became warm and crystals were formed; these were dissolved by heating with 2 ml of benzene, and to the hot solution was added 10 ml of petroleum ether (b. p. 30-60°); crystals (0.52 g) separated on cooling, m. p. 117°; after recrystallization from petroleum ether - m. p. 117.5°. Found: C 54.8, 54.6; H 7.6, 7.5; P 12.5, 12.6%.  $C_{22}H_{36}P_2N_2O_6$ . Calculated: C 54.3; H 7.4; P 12.7%.

The reaction of diethyl N-diethylphosphorylamidophosphate with diazomethane. An ether solution containing 0.12-0.15 M of diazomethane (obtained from nitrosomethylurea and dried for 3 hr over fused potassium hydroxide) was added dropwise at 15-20° with cooling to an ether solution of 17.4 g (0.06 M) of diethyl N-diethylphosphorylamidophosphate in 50 ml of absolute ether. An immediate decolorization of the solution was observed together with the evolution of nitrogen. When more than half of the solution of diazomethane had been added, the evolution of nitrogen ceased, and the solution remained yellow. On the following day the excess diazomethane and ether were removed in a vacuum. By distillation of the residue a fraction was isolated (13.6 g) with b. p. 98-106° (0.06 mm);  $n_D^{20}$  1.5355;  $d_4^{20}$  1.1564. Found: C 35.5, 35.7; H 7.5, 7.7; P 20.2, 20.4%.  $C_9H_{23}O_6NP_2$ . Calculated: C 35.6; H 7.6; P 20.4%. Since the mixture of isomers could not be separated, it was treated with hydrogen chloride.

The action of hydrogen chloride on the product of composition  $C_9H_{23}O_6NP_2$ . Dry hydrogen chloride was passed through 8 g of the product with composition  $C_9H_{23}O_6NP_2$  at 15-20°. Two fractions were isolated by distillation in vacuo: I - b. p. 52-55° (0.003 mm), 2.0 g; and II - b. p. 82-86° (0.003 mm);  $n_D^{20}$  1.4412;  $d_4^{20}$  1.2037; 4.6g.

Fraction I was distilled once more at 0.3 mm; b. p. 105-106°;  $n_D^{20}$  1.4372;  $d_4^{20}$  1.1664. Found: C 35.1, 35.4; H 7.9, 7.8; P 20.1, 20.0%.  $C_9H_{23}O_6NP_2$ . Calculated: C 35.6; H 7.6; P 20.4%. The data from the literature for the amide  $[(C_2H_5O)_2PO]_2NCH_3$  [2] are: b. p. 138-139° (3 mm);  $n_D^{20}$  1.4353;  $d_4^{20}$  1.1666.

The fraction appeared to be diethyl N-diethylphosphorylamidophosphate which had been obtained earlier [9] and had the following constants: b. p. 79-80° ( $1 \cdot 10^{-5}$  mm);  $n_D^{20}$  1.4415;  $d_4^{20}$  1.2029. The equivalent weight (thymolphthalein) was 290.5. The calculated equivalent weight of  $C_8H_{21}O_6NP_2$  is 289.2. The dibenzylamine salt (obtained by the procedure described above), m. p. 116.5-117°, gave a mixture melting point with the dibenzylamine salt of a known sample of diethyl N-diethylphosphorylamidophosphate of 116.5-117°.

The reaction of the diethyl N-diethylphosphorylamidophosphate with diazoethane. To a solution of 9 g (0.31 M) of diethyl N-diethylphosphorylamidophosphate in 20 ml of absolute ether was added dropwise an ether solution of diazoethane (approximately 0.05-0.06 M) with cooling. Nitrogen was evolved and the solution was bleached. Toward the end of the addition the solution remained orange. On the following day the diazoethane and ether were removed in vacuo. Triethyl N-diethylphosphorylimidophosphate 8.0 g (yield 81%) was isolated by vacuum distillation; b. p. 98° (0.1 mm);  $n_D^{20}$  1.4372;  $d_4^{20}$  1.1285. Found: C 38.3, 38.2; H 8.2, 8.2; P 18.9, 19.1%.  $C_{10}H_{25}O_6NP_2$ . Calculated: C 37.8; H 7.9; P 19.5%. The literature data for triethyl N-diethylphosphorylimidophosphate [9] are: b. p. 121° (0.5 mm);  $n_D^{20}$  1.4345;  $d_4^{20}$  1.1294.

The triethyl N-diethylphosphorylimidophosphate, 4 g, was treated with dry hydrogen chloride (15-20°). Diethyl N-diethylphosphorylamidophosphate, 2.8 g, was isolated; b. p. 86-89° ( $6 \cdot 7 \cdot 10^{-3}$  mm);  $n_D^{20}$  1.4412;  $d_4^{20}$  1.2002. The dibenzylamine salt of this material melted at 116.5-117°. A mixture melting point with the dibenzylamine salt of a known sample of diethyl N-diethylphosphorylamidophosphate melted at 116.5-117°.

Monodeuterated diethyl N-diethylphosphorylamidophosphate. This was obtained by dissolving 2.0 g of diethyl N-diethylphosphorylamidophosphate in 2.9 g of  $D_2O$ . On the following day the deuterium oxide was removed in vacuo at 2 mm, and was collected in a trap cooled to -60°. Monodeuterated diethyl N-diethylphosphorylamidophosphate was isolated by distillation of the residue; b. p. 77-78° ( $1 \cdot 10^{-4}$  mm);  $n_D^{20}$  1.4412. Found: C 33.3, 33.2; H + D 7.2, 7.3; P 20.8, 20.8%.  $C_8H_{20}DO_6NP_2$ . Calculated: C 33.1; H + D 7.6; P 21.3%.

Monodeuterated diethyl N-methylsulfonylamidophosphate. This was obtained by dissolving 0.1 g of diethyl N-methylsulfonylamidophosphate in 2.8 g of  $D_2O$ . After removal of the  $D_2O$  in vacuo, the residue was recrystallized from petroleum ether and melted at 96-96.5°. Found: C 25.9, 25.9; H + D 6.2, 6.3; P 13.2, 13.0; S 13.6, 13.6%.  $C_5H_{13}DO_5SNP$ . Calculated: C 25.9; H + D 6.5; P 13.3, 13.8%. The infrared spectra were made on an IKS-14 instrument. The cell thickness used for the liquid substances was 0.01 mm. The potassium bromide pressed disc method was used to obtain the spectra of the solid substances. (6 mg of the substance and 0.7 g of potassium bromide).

## SUMMARY

1. Diethyl N-acetylamidophosphate and the O-ethyl-N-acetylamidoalkylphosphinates ( $C_2H_5O$ ) $R$ PONHCOCH<sub>3</sub> ( $R = CH_3$  and  $C_2H_5$ ) were synthesized, and on the basis of the infrared spectral data conclusions were drawn about the amide structure of these substances.

2. On the basis of the infrared spectral data, it is suggested that diethyl N-diethylphosphorylamidophosphate and diethyl-N-methylsulfonylamido phosphate have the imide structure, in contrast to the N-alkyl- and N-acyl-amidophosphates which have the amide structure.

3. Diethyl N-diethylphosphorylamidophosphate reacted with diazomethane to form the products of both O- and N-methylation, but with diazoethane — only the O-ethylation product was attained.

## LITERATURE CITED

1. M. I. Kabachnik, The Chemistry and Application of Phosphorus-organic Compounds, Izd. AN SSSR, M., 1957, p. 78 [in Russian]; M. I. Kabachnik, T. A. Mastryukova, A. E. Shipov, and T. A. Melent'eva, Doklady Akad. Nauk SSSR, 124, 1061 (1959).
2. M. I. Kabachnik, Problems of the Mechanism of Organic Reactions, Kiev, 1954, p. 126 [in Russian].
3. Conant, J. Amer. Chem. Soc. 54, 4045 (1932).
4. W. Dieckman, Ber. 55, 2470 (1922).
5. K. H. Meyer, Ber. 45, 2854 (1912).
6. Yu. N. Sheinker, Doklady Akad. Nauk SSSR 83, 1081 (1957).
7. L. J. Bellamy and L. Beecher, J. Chem. Soc. 1952, 1701.
8. J. W. Anderson, J. Blodinger, and A. D. Welcher, J. Amer. Chem. Soc. 74, 5309 (1952).
9. M. I. Kabachnik and V. A. Gilyarov, in press, Izv. AN SSSR, Otd. Khim. Nauk.
10. L. Bellamy, The Infrared Spectra of Complex Molecules, John Wiley and Sons, 1958.
11. M. I. Kabachnik, V. A. Gilyarov, and E. N. Tsvetkov, Izv. AN SSSR, Otd. Khim. Nauk 1959, 2135.
12. B. A. Arbuzov, P. I. Alimov, M. A. Zvereva, I. D. Neklesova, and M. I. Kudrina, Izv. AN SSSR, Otd. Khim. Nauk 1954, 1047.
13. G. M. Kosolapoff and L. B. Reyne, J. Organ. Chem. 21, 413 (1956).

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. Some or all of this periodical literature may well be available in English translation. A complete list of the cover-to-cover English translations appears at the back of this issue.

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# THE CONDENSATION REACTION OF METHYLPHOSPHONIC ACID WITH $\alpha, \omega$ -DIETHOXYDIMETHYLSILOXANES

K. A. Andrianov, T. V. Vasil'eva, and L. M. Khananashvili

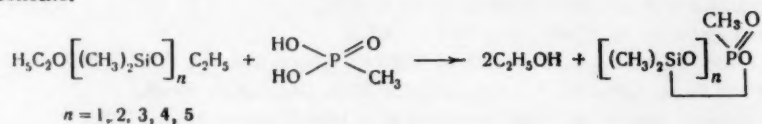
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The heterofunctional condensation reaction is widely used in the synthesis of organosilicon compounds. In the present work the condensation of  $\alpha, \omega$ -diethoxydimethylsiloxanes with methylphosphonic acid was studied. Experiments showed that this reaction is a convenient method also for the synthesis of mixed organosilicophosphorus compounds. The process goes preferentially in the direction of formation of cyclic products and not toward the formation of high-polymeric compounds as might be expected. Increase of the distance between alkoxy groups in  $\alpha, \omega$ -diethoxydimethylsiloxanes does not change the direction of the reaction. In all cases the reaction goes according to the following scheme:



Study of this reaction in the case of condensation of methylphosphonic acid with  $\alpha, \omega$ -diethoxydimethylsiloxanes having the general formula  $\text{C}_2\text{H}_5\text{O}[(\text{CH}_3)_2\text{SiO}]_n\text{C}_2\text{H}_5$  where  $n = 1-5$ , showed that the siloxane bond is not cleaved if  $n \leq 4$ .

In this case the resulting cyclic compounds contain as many dimethylsiloxane groups as there are in the original  $\alpha, \omega$ -diethoxydimethylsiloxane. Thus in the condensation of methylphosphonic acid with the  $\alpha, \omega$ -diethoxydimethylsiloxane where  $n = 3$ , hexamethylcyclomethylphosphonoxyltrisiloxane was isolated; with  $n = 4$ , octamethylcyclomethylphosphonoxyltetrasiloxane was obtained. In the condensation of methylphosphonic acid with the  $\alpha, \omega$ -diethoxydimethylsiloxane where  $n = 2$ , tetramethylcyclomethylphosphonoxylbisiloxane is formed. The condensation of methylphosphonic acid with dimethyldiethoxysilane leads to the formation of tetramethylcyclodimethylphosphonoxylbisiloxane.

In the condensation of methylphosphonic acid with the  $\alpha, \omega$ -diethoxydimethylsiloxane, where  $n = 5$ , the reaction proceeded with cleavage of the siloxane bond and formation of hexamethylcyclomethylphosphonoxyltrisiloxane, and only a small amount of decamethylcyclomethylphosphonoxypentasiloxane was isolated.

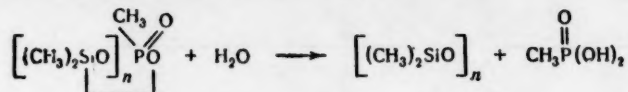
The compounds obtained are colorless, viscous liquids distillable in vacuo, which are easily hydrolyzed by atmospheric moisture. The main physicochemical properties of the synthesized compounds are given in Table 1.

In order to determine the composition and structure of the compounds obtained, not only analytical data for the first three compounds, but also their infrared absorption spectra were studied. The absorption spectra of hexamethylcyclomethylphosphonoxyltrisiloxane, tetramethylcyclomethylphosphonoxylbisiloxane, and tetramethylcyclodimethylphosphonoxylbisiloxane are shown in Figs. 1, 2, and 3. As is evident from Figs. 1-3, the following absorption bands occur: 2965, 2908, 1414, 312, and 815  $\text{cm}^{-1}$ , characteristic of the  $\text{CH}_3$  group; 1262  $\text{cm}^{-1}$ , characteristic of the  $\text{Si}-\text{CH}_3$  bond; 1200-1225  $\text{cm}^{-1}$ , characteristic of  $\text{P}=\text{O}$ ; 1040-1100  $\text{cm}^{-1}$ , characteristic of  $-\text{Si}-\text{O}-\text{Si}-$ .

The absorption spectra of hexamethylcyclomethylphosphonoxyltrisiloxane and tetramethylcyclodimethylphosphonoxylbisiloxane have an intense absorption band in the 1040-1100  $\text{cm}^{-1}$  region; tetramethylcyclomethylphosphonoxylbisiloxane has an absorption band with a maximum at  $\sim 1025 \text{ cm}^{-1}$ . For all three of the prepared compounds the 1000-1100  $\text{cm}^{-1}$  absorption bands apparently are superposed on absorption bands corresponding to the  $\text{Si}-\text{O}-\text{P}$  group. The absorption bands for the  $\text{Si}-\text{O}-\text{Si}$  bond lie in a region corresponding to that for cyclic compounds.



In order to confirm the structure of the prepared compounds, hexamethylcyclomethylphosphoxytrisiloxane, tetramethylcyclomethylphosphoxydisiloxane, and tetramethylcyclodi(methylphosphonoxy)disiloxane were hydrolytically cleaved and their hydrolysis products studied. The experiments showed that on treatment of the indicated compounds with water the following destructive reaction takes place:



The methylphosphonic acid formed was titrated with 0.1 N potassium hydroxide solution. Results are given in Table 2. The experiment showed that methylphosphonic acid is formed in quantities closely corresponding to the given equation.

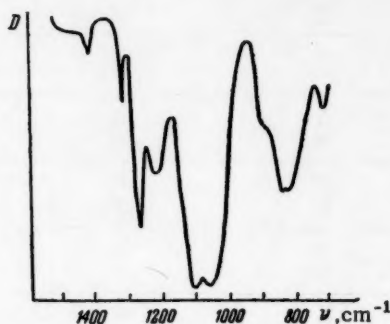


Fig. 1. IR absorption spectrum of hexamethylcyclomethylphosphoxytrisiloxane.

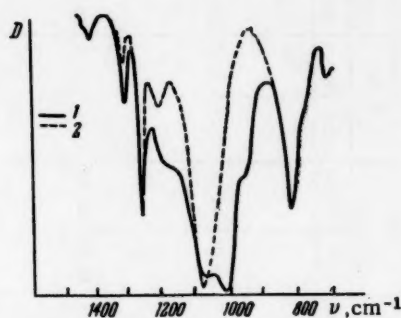


Fig. 2. IR absorption spectrum of tetramethylcyclomethylphosphoxydisiloxane (1) and its hydrolysis product (2).

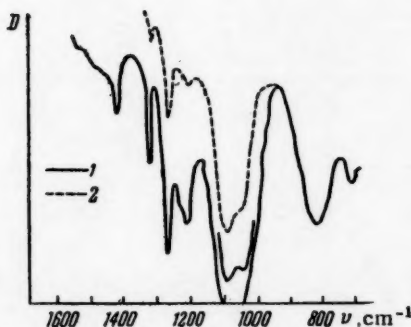


Fig. 3. IR absorption spectrum of tetramethylcyclodi(methylphosphonoxy)disiloxane (1) and its hydrolysis product (2).

On treatment of the methylcyclophosphoxysiloxanes, listed in Table 2, with water the mixture became turbid, and the reaction product then separated into two layers. Other hydrolysis products also were studied. In the case of tetramethylcyclomethylphosphoxydisiloxane it was found that the upper layer consisted of polydimethylcyclosiloxanes, whereas the lower layer was an aqueous solution of methylphosphonic acid, from which, after evaporation of the water, methylphosphonic acid crystals were isolated. The results of analysis of the hydrolysis products, are given in Table 3.

Moreover, the infrared absorption spectra of the hydrolysis products of tetramethylcyclomethylphosphoxydisiloxane and tetramethylcyclodi(methylphosphonoxy)disiloxane were studied. In Figs. 2 and 3 the dashed lines show the infrared absorption spectra of hydrolyzed tetramethylcyclomethylphosphoxydisiloxane and tetramethylcyclodi(methylphosphonoxy)disiloxane. In Fig. 2 a pronounced shift of the

absorption-band maximum from 1025 to 1081  $\text{cm}^{-1}$  is evident. This showed once more that in the course of hydrolysis the six-membered ring is converted to an eight-membered octamethylcyclotetrasiloxane, and the frequency of the Si-O-Si absorption band is shifted from 1025 to 1081  $\text{cm}^{-1}$ .

#### EXPERIMENTAL

Methylphosphonic acid, m. p. 104°, containing 30.27% phosphorus, was used for the preparation of the described compounds;  $\alpha, \omega$ -Diethoxydimethylsiloxanes were prepared by partial hydrolysis of dimethyldiethoxysilane. The constants of the compounds obtained corresponded to those given in the literature [1].

TABLE 1. Physicochemical Properties of Methylcyclomethylphosphoxysiloxanes

Compound	Formula	B, p, °C at 1-2 mm	$n_D^{20}$	$d_4^{20}$	MR		C, %		H, %		Si, %		P, %		Molecular Weight	
					calc.	found	calc.	found	calc.	found	calc.	found	calc.	found	calc.	found
Hexamethyl- cyclomethyl- phosphoxy- trisiloxane		134-136	1.4198	1.0925	69.86	69.58	28.00	27.73	7.03	7.05	28.09	27.91	10.28	10.25	300.4	295.0
Tetramethyl- cyclomethyl- phosphoxy- disiloxane		141-143	1.4232	1.1263	51.16	51.12	26.50	26.28	6.64	6.79	24.75	24.53	13.64	13.29	226.2	222.8
Tetramethyl- cyclodimethyl- phosphoxy- disiloxane		173-175	1.4415	1.2484	64.94	64.50	23.68	23.20	5.96	5.78	18.46	18.28	20.34	20.18	304.3	310.1
Octamethyl- cyclomethylphos- phoxytetra- siloxane		114-116	1.4189	1.0750	88.55	88.15	28.9	28.76	5.98	6.45	29.6	29.20	8.26	7.85	-	-
Decamethylcyclo- methylphos- phoxy-penta- siloxane		119-121	1.4227	1.0721	107.15	106.99	29.55	29.32	7.43	6.83	31.85	31.51	6.90	6.45	-	-

Synthesis of hexamethylcyclomethylphosphoxytrisiloxane. The reaction was carried out with a molar ratio of 1,3-diethoxyhexamethyltrisiloxane to methylphosphonic acid, equal to 1:1.2. The mixture was heated in a four-neck flask provided with a stirrer, thermometer, and straight condenser. The temperature in the liquid gradually rose to 100-110°. The alcohol that distilled off, amounted to 96% of theoretical. After driving off the alcohol, the reaction mixture was fractionated in vacuo. A product, boiling at 134-136° (1-2 mm), was isolated. The yield of hexamethylcyclomethylphosphoxytrisiloxane was 70% of theoretical.

TABLE 2. Number of Moles of Methylphosphonic Acid Obtained on Treatment of Dimethylcyclomethylphosphoxysiloxanes with Water

Compound	CH <sub>3</sub> PO <sub>4</sub> (OH) <sub>2</sub>	
	calculated	found
Hexamethylcyclomethylphosphoxytrisiloxane	1	0.99
Tetramethylcyclomethylphosphoxydisiloxane	1	0.97
Tetramethylcyclodi(methylphosphoxy)disiloxane	2	1.95

TABLE 3. Analysis of Tetramethylcyclomethylphosphoxydisiloxane Hydrolysis Products

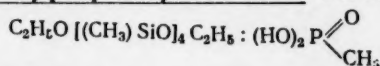
Polydimethylcyclosiloxanes			Methylphosphonic acid		
	calculated	found		calculated	found
C, %	32.42	32.55	P	32.25	32.13
H, %	8.15	8.20	M. p., °C	103	104
Si, %	37.9	37.2			

Synthesis of tetramethylcyclomethylphosphoxydisiloxane. The reaction was carried out with a molar ratio of 1,2-diethoxytetramethylsiloxane to methylphosphonic acid, equal to 1:1.2 under conditions similar to those of the preceding experiment. The alcohol that distilled off, amounted to 84% of theoretical. After driving off the alcohol the products were fractionated in vacuo. Tetramethylcyclomethylphosphoxydisiloxane, b. p. 141-143° (1-2 mm), was isolated. The yield was 40% of theoretical.

Synthesis of tetramethylcyclodi(methylphosphoxy)disiloxane. The reaction was carried out with a molar ratio of dimethyldiethoxysilane to methylphosphonic acid, equal to 1:1.5 under the conditions described for hexamethylcyclomethylphosphoxytrisiloxane.

The alcohol that distilled off, amounted to 85% of theoretical. Tetramethylcyclodi(methylphosphoxy)disiloxane distilled at 173-175° (1-2 mm). The yield was 33% of theoretical.

Synthesis of octamethylcyclomethylphosphoxytetrasiloxane. The reaction was carried out with the ratio



equal to 1:1.2. Octamethylcyclomethylphosphoxytetrasiloxane distilled at 114-116° (1-2 mm); the yield was 50% of theoretical.

Synthesis of decamethylcyclomethylphosphoxypentasiloxane. The reaction was carried out with a molar ratio of 1,9-diethoxydecamethylpentasiloxane to methylphosphonic acid, equal to 1:1.2 under the conditions described for hexamethylcyclomethylphosphoxytrisiloxane. At 119-121° (1-2 mm) decamethylcyclomethylphosphoxypentasiloxane and hexamethylcyclomethylphosphoxytrisiloxane distilled over in yields equal to 15 and 55% of theoretical, respectively.

Determination of methylphosphonic acid. A weighed sample (0.2-0.3 g) of the product was dissolved in 20 ml of water. To ensure quantitative hydrolysis the mixture was left for 15-20 hr. After this it was titrated with alkali in the presence of thymolphthalein. In this way the amount of methylphosphonic acid, formed on hydrolysis, was determined.

Analysis of the upper and lower layers of the hydrolysis product. The compounds obtained were hydrolyzed as described above. After this 5-8 ml of ether was added to the mixture; the latter then separated into two well-defined layers. The lower, water layer was poured into a casserole, the water evaporated, and the resulting crystals analyzed. The upper, ether layer was poured into a casserole, brought to constant weight in a vacuum cabinet, and analyzed.

The authors thank N. P. Gashnikova for taking the IR absorption spectra of the products obtained.

#### SUMMARY

1. The condensation reaction of methylphosphonic acid with  $\alpha,\omega$ -diethoxydimethylsiloxanes, leading to the formation of dimethylcyclomethylphosphonoxysiloxanes, was studied.
2. The properties of dimethylcyclomethylphosphonoxysiloxanes and their reactions with water were studied.

#### LITERATURE CITED

1. F. Hunter, J. Amer. Chem. Soc., 71, 2918 (1949).



# CIS-TRANS-DIPROPENYLMERCURY

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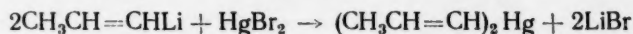
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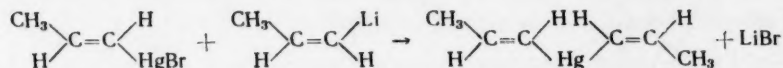
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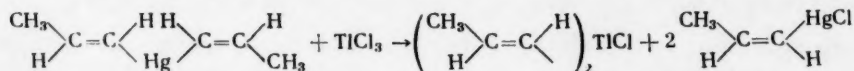
In our earlier article together with Nesmeyanov and Novikova [1] we described the synthesis of stereoisomers of di-(cis)- and di-(trans-propenyl)mercury from cis- and trans-propenylmercury bromide and conversions thereof, in which the configuration of the propenyl radical is retained, and gave a proof of the structures of these cis- and trans-isomers. The synthesis of di-(cis)- and di-(trans-propenyl)mercury from the corresponding propenyllithium stereoisomers and mercuric bromide according to the scheme



is set forth in the present article. Thus the resulting dipropenylmercury stereoisomers react with mercuric bromide without changing the configuration of the propenyl radical, and give cis- and trans-propenylmercury bromide, respectively. On the basis of the rule of nonalteration of the geometrical configuration in electrophilic and radical substitutions on the olefinic carbon [1, 2], I synthesized cis-trans-dipropenylmercury through the reaction of cis- or trans-propenylmercury bromide with trans- or cis-propenyllithium according to the scheme



As in the case of cis-trans-di(β-chlorovinyl)mercury [3], the exchange reaction of this substance with thallic chloride in ether led to pure cis-propenylmercury chloride containing no trace of the trans isomer, and also to pure di-(trans-propenyl)thallium chloride. Thallic chloride instantly exchanges two chlorine atoms for two trans-propenyl groups, whereas the cis-propenyl group remains bound to the mercury atom in cis-propenylmercury chloride.



An admixture of di-(cis)- and di-(trans-propenyl)mercury in the original substance would necessarily give, in this case, a mixture of the cis- and trans-isomers of the propenyl compounds of thallium and mercury. Thus this reaction provides cogent arguments in favor of the cis- and trans-configurations of propenyl groups bound to the mercury atom in our dipropenylmercury. Cis- and trans-propenylmercury bromides were isolated from the reaction products of cis-trans-dipropenylmercury and mercuric bromide by fractional crystallization.

Investigation of the IR spectrum showed that the dipropenylmercury has the vibration frequencies 920w and 1595s\* cm<sup>-1</sup> which characterize extra planar vibrations of the hydrogen atom and the C=C double bond of the cis-propenyl compound, whereas the vibration frequencies 980s and 1692s cm<sup>-1</sup> characterize this substance as the trans-propenyl compound of mercury [1]. The trans-series of olefinic compounds has intense vibration frequencies in the 950-980 cm<sup>-1</sup> region [4], and higher vibration frequencies in the region of the C=C bond than the cis-isomers. Therefore the results of investigation of the IR spectrum confirm our conclusion on the configuration. Moreover, propenylmercury acetate was synthesized in 91% of the theoretical yield through the reaction of di-(trans-propenyl)mercury with mercuric acetate in a benzene medium in the presence of traces of acetic acid.

\*s - strong; w - weak.

## EXPERIMENTAL

**Di-cis-propenylmercury.** To an ethereal solution of cis-propenyllithium, prepared at 5° from 1.146 g (0.1654 mole) of metallic lithium in 90 ml of dry ether and 10 g (0.0826 mole) of cis-propenyl bromide in 10 ml of ether, 7.84 g (0.0288 mole) of mercuric chloride in 8 ml of tetrahydrofuran was slowly added at 3-5°. After stirring for 2 hr at room temperature the reaction mass was decomposed with saturated ammonium chloride solution at 0-3°, washed with water (cold), and dried with fused calcium chloride. The solvent was completely distilled from the reaction product in vacuo at room temperature. The residue — a clear, liquid product — weighed 7 g; 85.5% of theoretical. Di-cis-propenylmercury had b. p. 79-80° (14 mm);  $n_D^{20}$  1.5628.

**Reaction of di-cis-propenylmercury with mercuric bromide.** To 3 g (0.0106 mole) of freshly-prepared, undistilled di-cis-propenylmercury in 10 ml of methanol, 3.82 g (0.0106 mole) of mercuric bromide in 9 ml of methanol was added. There was obtained 6.55 g (95%) of cis-propenylmercury bromide in the form of crystals with m. p. 60-62°. Recrystallization from ether did not change the melting point.

According to literature data, cis-propenylmercury bromide has m. p. 60-62° [1].

**Di-trans-propenylmercury.** To an ethereal solution of trans-propenyllithium, prepared at 3° from 2.2 g (0.317 mole) of metallic lithium in 150 ml of dry ether and 20 g (0.165 mole) of trans-propenyl bromide in 20 ml of ether, 15 g (0.0552 mole) of mercuric chloride in 15 ml of tetrahydrofuran was added dropwise at 3-10°. After stirring for 3 hr at room temperature the reaction product was decomposed (3-5°) with saturated ammonium chloride solution, washed with 50 ml of cold water, and dried with sodium sulfate. The solvent was completely distilled off in a water-jet-pump vacuum at 35°. The slightly-yellowish liquid residue weighed 13.8 g (88.2% of theoretical) and consisted of the known di-trans-propenylmercury [1].

**Reaction of di-trans-propenylmercury with mercuric bromide.** Solutions of 2.8 g (0.0099 mole) of freshly-prepared, undistilled di-trans-propenylmercury in 7 ml of methanol and 3.56 g (0.0099 mole) of mercuric bromide in 8 ml of methanol were mixed. Three g (94.6%) of theoretical of trans-propenylmercury bromide was isolated from the reaction mass, in the form of crystals with m. p. 119-120°. Recrystallization from ether did not change the melting point. Previously-described trans-propenylmercury bromide has m. p. 119-120° [1].

**Cis-trans-dipropenylmercury.** To an ethereal solution of trans-propenyllithium, prepared at 5-7° from 1.68 g (0.0138 mole) of trans-propenyl bromide in 6 ml of ether and 0.19 g (0.0273 mole) of metallic lithium in 40 ml of ether, cis-propenylmercury bromide in 15 ml of ether was added during 20 min (3-5°). After stirring for 2 hr at 10-15° the reaction product was decomposed with saturated ammonium chloride solution, washed with 15 ml of cold water, and dried with fused calcium chloride. The solvent was completely distilled off by means of a water-jet-pump at 25-30°. The residue, a liquid product, weighed 2.4 g (91% of theoretical);  $n_D^{20}$  1.5592. Found: C 26.48, 26.36; H 3.68, 3.74; Hg 69.40, 69.95%.  $C_6H_{10}Hg$ . Calculated: C 25.48; H 3.54; Hg 70.98%.

**Trans-propenylmercury acetate.** To 4 g (0.0141 mole) of di-trans-propenylmercury in 25 ml of benzene, 4.5 g (0.0141 mole) of mercuric acetate and 5 drops of glacial acetic acid were added. All the mercuric acetate dissolved within 5 min. A test sample did not give a reaction for mercuric ion with alkali. The reaction mass was concentrated to 2/3 volume, dried with fused sodium sulfate, filtered while warm, and diluted with 10 ml of petroleum ether; in this case a precipitate formed. The isolated and dried crystals weighed 6.7 g; m. p. 107-108°. An additional 1.3 g of the substance was obtained from the mother liquor. The total amount of the substance obtained was 8 g, which corresponds to 92.9% of theoretical. After recrystallization from a benzene-petroleum ether mixture (1:1), trans-propenylmercury acetate had m. p. 111°; it decomposed at 135°. Found: C 19.8, 19.6; H 2.88, 2.81; Hg 66.47%.  $C_5H_8HgO_2$ . Calculated: C 19.90; H 2.66; Hg 66.7%.

**Reaction of cis-trans-dipropenylmercury with thallic chloride.** To 1 g (0.0176 mole) of freshly-prepared cis-trans-dipropenylmercury in 10 ml of dry ether, 0.54 g (0.00353 mole) of thallic chloride in 5 ml of ether was added with stirring. After 0.5 hr the resulting white precipitate was filtered out, washed with ether, and dried; weight 0.53 g (93% of theoretical). After recrystallization from pyridine the acicular crystals of di-trans-propenylthallium chloride decomposed above 340°. According to literature data [1]; decomposition temperature above 340°. Found: C 22.65, 22.25; H 2.90, 3.05%.  $C_6H_{10}TlCl$ . Calculated: C 22.38; H 3.13%.

The solvent was distilled from the main filtrate, and the solid residue was recrystallized from methanol. There was obtained 0.91 g (93% of theoretical) of cis-propenylmercury chloride, m. p. 88-91°. A mixture test with known, prepared cis-propenylmercury chloride gave no melting-point change.

Reaction of cis-trans-dipropenylmercury with mercuric bromide. A 0.3 g (0.001 mole) quantity of cis-trans-dipropenylmercury in 2 ml of methanol and 0.38 g (0.001 mole) of mercuric bromide in 2.5 ml of methanol were mixed at room temperature. After 10 min the mixture was cooled (ice water), and the crystals which separated were filtered out and recrystallized. The following fractions were isolated: I - m. p. about 88°, 0.2 g; II - m. p. about 76°, 1.2 g; III - m. p. 56-60°, 0.18 g.

Trans-propenylmercury bromide, m. p. 123-124°, was isolated from fractions I and II by crystallization from fractions I and II by crystallization from petroleum ether; cis-propenylmercury bromide, m. p. 60-61°, was similarly isolated from fraction III. Trans-propenylmercury bromide, described in the literature [1], has m. p. 123-124°, whereas its cis-isomer melts at 60-61°.

#### SUMMARY

1. The synthesis of an organomercury compound containing two stereoisomeric propenyl groups, one with the cis- and the other with the trans-configuration, was carried out in the case of dipropenylmercury.
2. The configuration of the dipropenylmercury obtained, was determined by chemical and physical methods.
3. It is suggested that benzene be used as solvent in the synthesis of acetyl derivatives of mercury through the reaction of fully-substituted mercury compounds with mercuric acetate.

#### LITERATURE CITED

1. A. N. Nesmeyanov, A. E. Borisov, and N. V. Novikova, *Izv. AN SSSR, Otd. Khim. Nauk* **1959**, 1216.
2. A. N. Nesmeyanov and A. E. Borisov, *Doklady Akad. Nauk SSSR* **60**, 67 (1948).
3. A. N. Nesmeyanov, A. E. Borisov, and R. I. Shepeleva, *Izv. AN SSSR, Otd. Khim. Nauk* **1949**, 583.
4. R. S. Rasmussen and R. R. Brattain, *J. Chem. Phys.* **15**, 120 (1947); N. Sheppard and D. M. Simpson, *Quart. Rev.* **6**, 24 (1952).

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. Some or all of this periodical literature may well be available in English translation. A complete list of the cover-to-cover English translations appears at the back of this issue.

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# REACTION OF ASYMMETRIC ORGANOMERCURY COMPOUNDS WITH THALLIUM TRICHLORIDE

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We had observed a difference in the exchange rates of the *cis*- and *trans*- $\beta$ -chlorovinyl groups when *cis*-*trans*-bis( $\beta$ -chlorovinyl)mercury is reacted with thallium trichloride [1]. It was also established that the *trans*-isomers of organometallic compounds containing an olefinic hydrocarbon radical react with thallium trichloride and tribromide much more rapidly than do the *cis*-isomers [2, 3]. If it is assumed, as we had done with a substantial degree of certainty, that replacement of metal by metal is accomplished as the result of electrophilic attack by the metal halide on the radical of the asymmetric compound, then it follows that the radicals of *trans*-structure are more electronegative and in the Kharasch series are located to the left of their *cis*-isomers. It seemed of undoubted interest to expand the study of behavior in the reaction with  $TlCl_3$  to a wider orbit of asymmetric organomercury compounds for the purpose of comparing a series of radicals, arranged in the order of their ease of cleavage in this reaction, with the Kharasch series, where the hydrogen ion serves as the radical-cleaving reagent.

For this purpose we synthesized a series of asymmetric organomercury compounds, starting with the organolithium [4] and organomagnesium [5] compounds and employing the method developed by Nesmeyanov, Kocheshkov, and Freidlina [6], and investigated their exchange reaction with thallium trichloride, proceeding in accordance with the scheme:

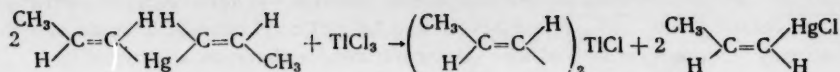


Analogous to *cis*-*trans*-bis( $\beta$ -chlorovinyl)mercury [1], *cis*-*trans*-dipropenylmercury reacts with thallium trichloride to yield only the *trans*-dipropenylthallium chloride in 93% of the theoretical yield, with none of the *cis*-isomer as impurity, while the *cis*-propenyl radical remains attached to the mercury atom as *cis*-propenylmercury chloride:

Data on the Reaction of Asymmetric Organomercury Compounds with Thallium Trichloride

Formula of starting compound	Reaction products isolated	
	Organothallium compound	Organomercury compound
$\begin{array}{c} Cl \\ \diagdown \\ C=C \\ \diagup \\ H \end{array} \begin{array}{c} H \\ \diagup \\ C \\ \diagdown \\ Hg \end{array} \begin{array}{c} H \\ \diagup \\ C \\ \diagdown \\ Cl \end{array}$	$\left( \begin{array}{c} Cl \\ \diagdown \\ C=C \\ \diagup \\ H \end{array} \right)_2 TlCl$	$\begin{array}{c} Cl \\ \diagdown \\ C=C \\ \diagup \\ H \end{array} \begin{array}{c} H \\ \diagup \\ C \\ \diagdown \\ HgCl \end{array}$
$\begin{array}{c} CH_3 \\ \diagdown \\ C=C \\ \diagup \\ H \end{array} \begin{array}{c} H \\ \diagup \\ C \\ \diagdown \\ Hg \end{array} \begin{array}{c} H \\ \diagup \\ C \\ \diagdown \\ CH_3 \end{array}$	$\left( \begin{array}{c} CH_3 \\ \diagdown \\ C=C \\ \diagup \\ H \end{array} \right)_2 TlCl$	$\begin{array}{c} CH \\ \diagdown \\ C=C \\ \diagup \\ H \end{array} \begin{array}{c} H \\ \diagup \\ C \\ \diagdown \\ HgCl \end{array}$
$C_2H_5HgC_3H_5$	$(C_6H_5)_2TlCl$	$C_2H_5HgCl$
$C_2H_5HgC_{10}H_7-\alpha$	$(\alpha-C_{10}H_7)_2TlCl$	$C_2H_5HgCl$
$C_6H_5HgC_{10}H_7-\alpha$	$(C_6H_5)_2TlCl + C_6H_5TlCl_2$	$\alpha-C_{10}H_7HgCl$
$o-CH_3OC_6H_4HgC_{10}H_7-\alpha$	$(o-CH_3OC_6H_4)_2TlCl$	$\alpha-C_{10}H_7HgCl$
$(CH_3)_3C_6H_2HgC_{10}H_7-\alpha$	$(\alpha-C_{10}H_7)_2TlCl$	$(CH_3)_3C_6H_2HgCl$
$o-CH_3OC_6H_4HgC_6H_5$	$(o-CH_3OC_6H_4)_2TlCl$	$C_6H_5HgCl$
$C_4H_9HgCH_2C_6H_5$	$TlCl$	$C_4H_9HgCl + C_6H_5CH_2HgCl$





The cases observed by us earlier by reacting asymmetric organomercury compounds, containing stereoisomeric olefin radicals, with thallium trichloride have been summarized in one table along with the experimental material described in this paper.

As a result, study revealed that thallium trichloride exchanges two of its chlorine atoms for those radicals attached to the mercury atom that are subjected to electrophilic attack by the hydrogen ion in the decomposition of  $\text{RHgR}'$  with hydrochloric acid [7], with the exception of phenyl- $\alpha$ -naphthylmercury, which deviates from this rule.

## EXPERIMENTAL

The reaction of *cis-trans*-dipropenylmercury with thallium trichloride was described in a previous paper [4].

**Reaction of ethylphenylmercury with thallium trichloride.** With cooling (ice + water), 2.5 g (0.008 mole) of thallium trichloride in ether solution was added to 5 g (0.016 mole) of ethylphenylmercury [7] in 50 ml of absolute ether. The obtained precipitate was filtered, washed with ether, and then with acetone. After recrystallization from pyridine, the obtained diphenylthallium chloride did not melt up to 310°; weight 2.35 g (75% of theory). Found: C 37.20, 37.08; H 2.64, 2.58%.  $\text{C}_{12}\text{H}_{10}\text{TiCl}$ . Calculated: C 36.57; H 2.56%. From the filtrate we isolated 3.52 g (81.7% of theory) of ethylmercury chloride with m. p. 192-193°. The mixed melting point with authentic ethylmercury chloride was not depressed.

**Reaction of ethyl- $\alpha$ -naphthylmercury with thallium trichloride.** With cooling, a solution of 2 g (0.0056 mole) of ethyl- $\alpha$ -naphthylmercury in 50 ml of absolute ether was mixed with an ether solution of 1.72 g (0.0027 mole) of thallium trichloride. The obtained precipitate of di- $\alpha$ -naphthylthallium chloride was filtered immediately, washed with ether, and dried; weight 1.34 g (97.1% of theory); after recrystallization from pyridine it did not melt up to 310°. Found: C 48.37, 48.38; H 3.0, 2.91%.  $\text{C}_{20}\text{H}_{14}\text{TiCl}$ . Calculated: C 48.6; H 2.86%.

After evaporation of the ether we obtained 1.06 g (88.2%) of ethylmercury chloride, which after recrystallization from alcohol had m. p. 191-192°. The mixed melting point with authentic ethylmercury chloride was not depressed.

**Reaction of phenyl- $\alpha$ -naphthylmercury with thallium trichloride.** a) With cooling, a solution of 0.7 g (0.0017 mole) of phenyl- $\alpha$ -naphthylmercury in 300 ml of absolute ether was mixed with an ether solution of 0.537 g (0.0017 mole) of thallium trichloride. After 30 min the ether was removed by distillation, and the residue was boiled with water. The hot aqueous solution was separated from the precipitate, which after recrystallization from benzene had m. p. 188-189°; weight 0.4 g (64.5%). The mixed melting point with authentic  $\alpha$ -naphthylmercury chloride was not depressed. From the aqueous solution we isolated 0.38 g (62.3%) of phenylthallium dichloride with m. p. 240-242°. According to the literature [8]: m. p. 240°.

b) A solution of 1.3 g (0.0032 mole) of phenyl- $\alpha$ -naphthylmercury in 25 ml of dry dioxane was mixed with an ether solution of 0.61 g (0.0019 mole) of thallium trichloride. The next day the obtained precipitate of diphenylthallium chloride was filtered, washed with ether, and dried. After recrystallization from pyridine it decomposed at 310°; weight 0.5 g (79.3%). Found: C 36.41, 36.57; H 2.61, 2.63%.  $\text{C}_{12}\text{H}_{10}\text{TiCl}$ . Calculated: C 36.57; H 2.56%.  $\alpha$ -Naphthylmercury chloride was isolated from the filtrate; after recrystallization from benzene it melted at 188-189°; weight 0.96 g (76%). The mixed melting point with authentic  $\alpha$ -naphthylmercury chloride was not depressed.

**Reaction of  $\alpha$ -naphthyl-o-anisylmercury with thallium trichloride.** A solution of 0.63 g (0.0014 mole) of  $\alpha$ -naphthyl-o-anisylmercury, m. p. 223-225°, in 20 ml of dry dioxane was mixed at 40° with an ether solution of 0.22 g (0.0007 mole) of thallium trichloride. The next day the dioxane was distilled off using a water-jet pump. The remaining solid residue (0.8 g) was treated with hot alcohol. Here the insoluble portion of the precipitate was di-o-anisylthallium chloride; weight 0.25 g (80.7%); after recrystallization from alcohol, m. p. 269° (decompn.). Found: C 36.93; H 3.09%.  $\text{C}_{14}\text{H}_{14}\text{O}_2\text{TiCl}$ . Calculated: C 37.03; H 3.11%.

From the alcohol solution we isolated  $\alpha$ -naphthylmercury chloride with m. p. 188-189°; weight 0.44 g (86.27%). The mixed melting point with authentic  $\alpha$ -naphthylmercury chloride was not depressed.

**Synthesis of o-anisylbutylmercury.** o-Anisylmercury bromide was added in small portions, at 25-30°, to the Grignard reagent obtained from 0.47 g of magnesium and 2.8 g of butyl bromide in 50 ml of absolute ether. All of the o-anisylmercury bromide went into solution. After this the reaction mass was stirred for 3.5 hr at 25-30°. The next day the reaction mass was decomposed with a saturated solution of ammonium chloride to 1-5°. After drying over calcined sodium sulfate, the solvent was removed using a water-jet pump and the residue, an oil, was shown to contain mercury but gave a negative test for halogen; weight 2 g (60%). The obtained o-anisylbutylmercury was decomposed with alcoholic hydrochloric acid solution. Here butylmercury chloride was isolated in 93.8% yield, m. p. 128-129°. According to [9]: m. p. 130°. Found: C 36.63; H 4.9%.  $C_{11}H_{16}OHg$ . Calculated: C 36.20; H 4.4%.

**Reaction of mesityl- $\alpha$ -naphthylmercury with thallium trichloride.** A solution of 0.5 g (0.00112 mole) of mesityl- $\alpha$ -naphthylmercury, m. p. 180-181°, in 35 ml of a 1:1 mixture of absolute ether and toluene was mixed with an ether solution of 0.18 g (0.00057 mole) of thallium trichloride. After 30 min the obtained precipitate of di- $\alpha$ -naphthylthallium chloride was filtered; weight 0.21 g (75%). Found: C 48.10, 48.02; H 2.94, 2.94%.  $C_{20}H_{14}TlCl$ . Calculated: C 48.6; H 2.86%. Mesitylmercury chloride, m. p. 198°, was isolated from the filtrate; weight 0.35 g (89.7%). From the literature [10]: m. p. 200°.

**Reaction of o-anisylbutylmercury with thallium trichloride.** An ether solution of 0.21 g (0.00068 mole) of thallium trichloride was added at room temperature to 0.5 g (0.00137 mole) of o-anisylbutylmercury in 6 ml of absolute ether. After 30 min the obtained precipitate was filtered and washed with ether. After recrystallization from alcohol, we obtained 0.25 g (83.3%) of di-o-anisylthallium chloride with m. p. 269° (decompn.). Found: C 36.90, 36.93; H 3.13, 3.09%.  $C_{14}H_{14}O_2TlCl$ . Calculated: C 37.03; H 3.11%.

Butylmercury chloride was isolated from the ether solution, and after recrystallization from alcohol melted at 128-129°; weight 0.35 g (85.2%). The mixed melting point with authentic butylmercury chloride was not depressed.

**Reaction of benzylbutylmercury with thallium trichloride.** A solution of 4.5 g (0.013 mole) of benzylbutylmercury in 30 ml of absolute ether was cooled to -5° and then mixed with an ether solution of 2.07 g (0.0066 mole) of thallium trichloride. The obtained precipitate of thallium chloride was filtered and dried. Weight 1.53 g (50%). Evaporation of the ether gave 2.3 g of residue, from which on standing we isolated 1.31 g of butylmercury chloride, which after recrystallization from ethanol had m. p. 128-129°. The mixed melting point with authentic butylmercury chloride was not depressed.

The liquid residue from the butylmercury chloride was vacuum-distilled to yield a substance that after recrystallization from ethanol had m. p. 103-104°. The mixed melting point with authentic butylmercury chloride was not depressed.

#### SUMMARY

Thallium trichloride exchanges two of its halogen atoms only for a radical that possesses a trans-configuration in cis-trans compounds, or for a radical that experiences electrophilic attack by the hydrogen ion in the decomposition of  $RHgR'$  by hydrochloric acid.

#### LITERATURE CITED

1. A. N. Nesmeyanov, A. E. Borisov, and R. I. Shepeleva, *Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk* **1949**, 582.
2. A. E. Borisov, V. D. Vil'chevskaya, and A. N. Nesmeyanov, *Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk* **1954**, 1011.
3. A. N. Nesmeyanov, A. E. Borisov, and N. V. Novikova, *Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk* **1959**, 1222.
4. A. E. Borisov, *Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk* **1961**, 1036.
5. M. S. Kharasch and A. L. Flenner, *J. Amer. Chem. Soc.* **54**, 674 (1932).
6. A. N. Nesmeyanov, K. A. Kocheshkov, and R. Kh. Freidlina, *Zhur. Obshchei Khim.* **5**, 1171 (1935).
7. M. S. Kharasch and R. Marker, *J. Amer. Chem. Soc.* **48**, 3130 (1926).
8. N. N. Mel'nikov and G. P. Gracheva, *Zhur. Obshchei Khim.* **5**, 1786 (1935).
9. C. S. Marvel and V. L. Gould, *J. Amer. Chem. Soc.* **44**, 156 (1922).
10. A. Michaelis, *Ber.* **28**, 592 (1895).

# SYNTHESIS OF ORGANOMERCURY NITRO COMPOUNDS

## COMMUNICATION 4. ADDITION OF MERCURY SALT OF TRINITROMETHANE

### TO UNSATURATED HYDROCARBONS

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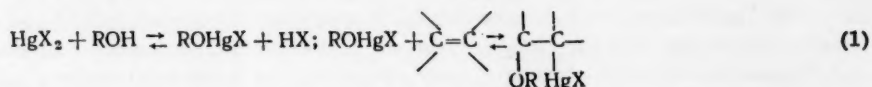
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Original article submitted July 19, 1960

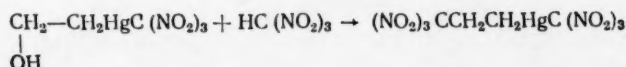
In previous communications [1-3] we have shown that the mercury salt of trinitromethane can be used successfully for the mercuriation of various aliphatic, alicyclic, aromatic and heterocyclic compounds to yield substances with the general formula  $R-Hg-C(NO_2)_3$ . In addition, it was established [4] that the reaction of this salt with the nitro derivatives of aromatic compounds leads to the formation of complex addition products of 1:1 composition, for example, in the case of nitrobenzene the complex  $NO_2C_6H_5 \cdot Hg[C(NO_2)_3]_2$ . A study of these reactions revealed both a certain similarity and a difference in the chemical behavior of the mercury salt of trinitromethane when compared with the usual mercurating agents. For this reason it seemed of interest to us to continue a study of the properties of this peculiar organomercury compound in reactions characteristic for mercuric salts and, first, in the reaction of addition to the double bond.

As is known, in solvents of general formula ROH a number of mercury salts add to olefins with the formation of either  $\beta$ -mercurated alcohols or ethers. At the present time it has been shown that this reaction goes with the prior hydrolysis (alcoholysis) of the mercury salt in accordance with the scheme

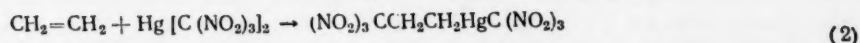


and represents stepwise electrophilic addition to the double bond [5]. A study of the reactions of the mercury salt of trinitromethane with olefins was started by us with a study of the addition reactions of this salt to ethylene in aqueous and in alcohol solutions. It was established that the reaction product is not  $\alpha$ -trinitromethylmercuri- $\beta$ -hydroxyethane (or the corresponding ether), the formation of which was to be expected if the reaction went in accordance with (1), but instead it is 1,1,1-trinitro-3-(trinitromethylmercuri)propane,  $(NO_2)_3CCH_2CH_2HgC(NO_2)_3$ .

It could be postulated that the formation of this compound goes either through the stage of the  $\beta$ -mercurated alcohol (ether) in accordance with (1) [where  $X = C(NO_2)_3$ ], with subsequent replacement of the hydroxyl (alkoxyl) group by the trinitromethyl radical:



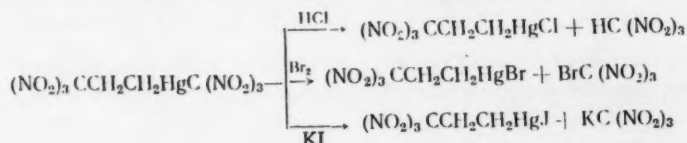
or by the direct addition of the elements of the trinitromethane mercury salt to the double bond:



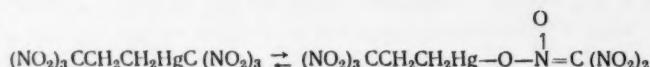
To answer this question, we studied the reaction of the mercury salt of trinitromethane with ethylene in solvents, not containing hydroxyl (alkoxyl) groups. It proved that when the mercury salt of trinitromethane is reacted with ethylene in either nitromethane or nitrobenzene medium, i.e., solvents that exclude the possibility of forming the  $\beta$ -mercurated alcohol (ether) as an intermediate, the reaction product is again 1,1,1-trinitro-3-(trinitromethylmercuri)propane. This may be considered as proof that the formation of this compound takes place by the direct addition of the mercury salt of trinitromethane to ethylene (2). This type of addition of mercury salts to the double

bond of olefins is a new reaction in the chemistry of organomercury compounds. The reaction is run at room temperature (18–20°), passing a stream of ethylene into a water solution of the mercury salt of trinitromethane for 7–8 hr; the yield of the end product is 95–98%. 1,1,1-Trinitro-3-(trinitromethylmercuri)propane is a colorless crystalline substance. A characteristic yellow color appears when it is dissolved in either alcohol or acetone; the solutions in dry ether or benzene are colorless.

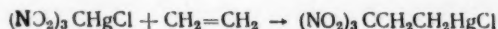
The reaction of 1,1,1-trinitro-3-(trinitromethylmercuri)propane with acids, halogens, and halide salts goes with a replacement of the trinitromethyl radical attached to the mercury atom:



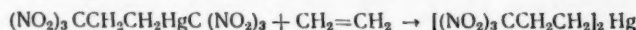
Both the fact that colored solutions arise and the above presented reactions indicate that this trinitromethyl radical is capable of tautomeric transformations, analogous to those observed for the mercury salt of trinitromethane and for the mercuriation products obtained by us [1, 2]. As a result, 1,1,1-trinitro-3-(trinitromethylmercuri)propane, being in the dry state and in nonpolar solvents a true organometallic compound, in polar solvents acquires a saltlike character, becoming a derivative of the aci-form of trinitromethane:



Because of the poor solubility of the true organometallic compound in water, the equilibrium between the two tautomeric forms in water solutions is shifted almost completely toward the side of the organometallic compound. This shift progresses with time, and the formation of 1,1,1-trinitro-3-(trinitromethylmercuri)propane is observed even 5–6 hr after the termination of ethylene passage. Acidification of the reaction mixture with trinitromethane accelerates the formation of the organometallic compound noticeably.\* On the other hand, increasing the temperature favors some shift of the equilibrium between the two tautomeric forms toward the formation of the energetically less favorable aci-form. This circumstance made it possible to recrystallize 1,1,1-trinitro-3-(trinitromethylmercuri)propane from water. It is interesting to mention that the obtained compounds, containing the trinitropropyl radical, exhibit under the influence of the nitro group a sharp increase in the stability of the bond between the mercury atom and the carbon of the trinitropropyl grouping. For example, 1,1,1-trinitro-3-(chloromercuri)propane remains unchanged even when heated with concd. hydrochloric acid in sealed ampoules at 100° for 12 hr; it also fails to react with bromine or chlorine. Further study revealed that not only the mercury salt of trinitromethane itself, but, in general, also compounds of type  $\text{RHgC(NO}_2\text{)}_3$  are capable of adding to the double bond. Thus, chloromercuritrinitromethane, formed by reacting trinitromethane with aqueous mercuric chloride solution, gives 1,1,1-trinitro-3-(chloromercuri)propane when reacted with ethylene:



Also of great interest is the ability of 1,1,1-trinitro-3-(trinitromethylmercuri)propane to add to a second molecule of ethylene, giving the symmetrical bis(trinitropropyl)mercury:



Ethylene is passed into a solution of 1,1,1-trinitro-3-(trinitromethylmercuri)propane at room temperature.\*\* Here it is specifically the addition reaction that takes place, and not the spontaneous symmetrization of the starting organomercury compound, since in the absence of ethylene the formation of bis(trinitropropyl)mercury is not observed.

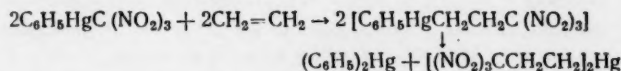
\* Increasing the hydrogen-ion concentration favors transition of the aci-form of trinitromethane to the true form. The absorption spectrum of trinitromethane in sulfuric acid solution is analogous to the spectrum of the pseudo acid in chloroform solution [6].

\*\* The reaction may be run in any polar solvents (alcohols, nitrobenzene, etc.), in which the 1,1,1-trinitro-3-(trinitromethylmercuri)propane is soluble. It should be mentioned that in these solvents it is possible to obtain bis(trinitropropyl)mercury directly from the mercury salt of trinitromethane, not isolating the 1,1,1-trinitro-3-(trinitromethylmercuri)propane; the reaction time is 12 hr.



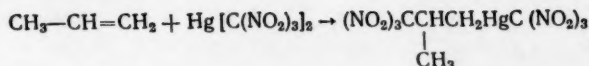
Similar to 1,1,1-trinitro-3-(chloromercuri)propane, this compound remains unchanged when heated with concd. mineral acids (except  $\text{HNO}_3$ ,  $d = 1.5$ ), it fails to react with either chlorine or bromine, and it is completely insoluble in water.

Further it was shown that (trinitromethyl)phenylmercury also adds readily to ethylene. However, in this case the reaction products proved to be diphenylmercury and bis(trinitropropyl)mercury, the formation of which can be explained by the disproportionation of the unsymmetrical addition product:

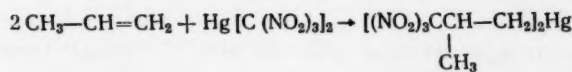


Reaction of the mercury salt of trinitromethane with ethylene, the same as mercuration with this salt, occurs only in polar solvents. As a result, also in this reaction the aci-form of the salt proves to be the operating source. The addition of the mercury salt of trinitromethane to the double bond was studied by us further on the examples of propylene, styrene, cyclopentene, and cyclohexene. In all cases the reaction goes by the same scheme as in the case of ethylene. Most of the obtained compounds are crystalline products.

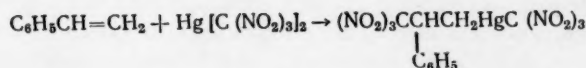
Propylene reacts with an aqueous solution of the mercury salt of trinitromethane, forming 1,1,1-trinitro-2-methyl-3-(trinitromethylmercuri)propane.



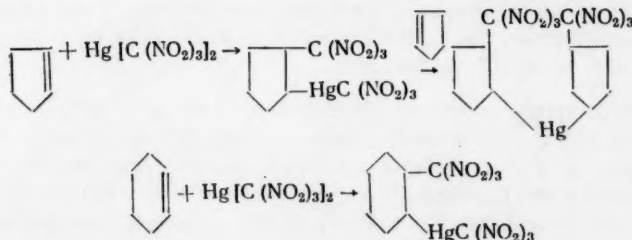
If the reaction is run in alcohol the corresponding symmetrical compound - bis(1,1,1-trinitro-2-methylpropyl)mercury - is obtained.



Reaction of the mercury salt of trinitromethane with styrene leads to the formation of 1,1,1-trinitro-2-phenyl-3-(trinitromethylmercuri)propane. The corresponding symmetrical compound



is a viscous oil. The reaction of the mercury salt of trinitromethane with cyclopentene and cyclohexene does not go as completely as when the reaction is with an olefin having a terminal methylene group. In the case of cyclopentene, both the symmetrical and the unsymmetrical addition products are crystalline compounds. The reaction with cyclohexene leads to only one crystalline product, namely 1-trinitromethyl-2-(trinitromercuri)cyclohexane.



In their chemical properties, the products obtained by the addition of the mercury salt of trinitromethane to the above enumerated unsaturated hydrocarbons are analogous to the corresponding ethylene derivatives. The mercury salt of trinitromethane does not react with iso-olefins, having even one quaternary carbon atom at the double bond. Thus, for example, isobutylene does not react with the salt either in water or in alcohol solution.

## EXPERIMENTAL

Preparation of water solution of mercury salt of trinitromethane. Trinitromethane (200 g) was added in small portions (10-15 ml each) to a vigorously stirred suspension of 140 g of freshly prepared mercuric oxide in 1200 ml of water. The mercuric oxide gradually went into solution, yielding toward the end of reaction a clear solution of the mercury salt of trinitromethane. The pH of the salt solution should not exceed 2.

Reaction of mercury salt of trinitromethane with ethylene in aqueous medium. A stream of ethylene was passed at room temperature into a water solution of the mercury salt of trinitromethane (10 g in 50 ml of water), contained in a graduated cylinder. A precipitate of 1,1,1-trinitro-3-(trinitromethylmercuri)propane deposited within 15-20 min after the start of reaction. The total time of ethylene passage was 6 hr, and the precipitate was filtered at 2 hr intervals. Then the reaction mixture was allowed to stand for 12 hr, and here an additional amount of product deposited. Each portion of the filtered precipitate was washed 2-3 times with water and then air-dried. The total yield was 9.8 g (93% of theory); m. p. 167° (with decomposition, allowed to crystallize slowly from water). Found: C 8.97, 9.13; H 0.79, 0.82; N 15.96, 15.97%; mole wt. 528.1.  $C_4H_4N_6O_{12}Hg$ . Calculated: C 9.09; H 0.76; N 15.99%; mole wt. 528.73.

The treatment of 1,1,1-trinitro-3-(trinitromethylmercuri)propane with 6 N hydrochloric acid at room temperature gave 1,1,1-trinitro-3-(chloromercuri)propane; yield 90% of theory; m. p. 142° (from chloroform). Found: Cl 8.65, 8.73%.  $C_3H_4N_3O_6HgCl$ . Calculated: Cl 8.56%.

The reaction of 1,1,1-trinitro-3-(trinitromethylmercuri)propane with bromine in chloroform solution gave 1,1,1-trinitro-3-(bromomercuri)propane in 81% yield; m. p. 128-129° (from chloroform). Found: C 8.03, 8.13; H 1.09, 1.17; N 9.42, 9.53%.  $C_3H_4N_3O_6HgBr$ . Calculated: H 0.88; N 9.46%.

1,1,1-Trinitro-3-(trinitromethylmercuri)propane is converted to 1,1,1-trinitro-3-(iodomercuri)propane by reaction with potassium iodide in aqueous-alcohol solution; yield 73% of theory; m. p. 102° (from 75% ethyl alcohol).

Reaction of trinitromethane with ethylene in the presence of mercuric chloride. A stream of ethylene was passed for 40 hr at room temperature into a saturated water solution of equimolar amounts of trinitromethane and mercuric chloride. The obtained precipitate of 1,1,1-trinitro-3-(chloromercuri)propane was filtered, air-dried, and recrystallized from chloroform; m. p. 142°; yield 80% of theory.

Reaction of mercury salt of trinitromethane with ethylene in nitromethane. A stream of ethylene was passed for 2 hr into a solution of 10 g of the mercury salt of trinitromethane in 20 ml of dry nitromethane. The nitromethane was vacuum-distilled. The residual precipitate, being a mixture of 1,1,1-trinitro-3-(trinitromethylmercuri)propane and bis(trinitropropyl)mercury, was separated by recrystallization from water. Here the water-insoluble portion was bis(trinitropropyl)mercury (m. p. 155°, from chloroform). 1,1,1-Trinitro-3-(trinitromethylmercuri)propane was isolated from the water filtrate and had m. p. 167°.

Reaction of mercury salt of trinitromethane with ethylene in alcohol medium. A stream of ethylene was passed for 12 hr at room temperature into a solution of 10 g of the mercury salt of trinitromethane in 30 ml of ethyl alcohol. After 1-1.5 hr, crystals of bis(trinitropropyl)mercury began to separate from the solution; on conclusion of reaction the crystals were filtered, washed with a little alcohol, and then several times with water. Dilution of the filtrate with water gave an additional amount of bis(trinitropropyl)mercury. Total yield 9.4 g (84% of theory). After two recrystallizations from chloroform, m. p. 155° (decompn.). Found: C 12.73, 12.86; H 1.44, 1.49; N 14.82, 15.06%.  $C_6H_8N_6O_{12}Hg$ . Calculated: C 12.94; H 1.45; N 15.09%.

Reaction of (trinitromethyl)phenylmercury with ethylene. A stream of ethylene was passed for 4 hr at room temperature into a solution of 2 g of (trinitromethyl)phenylmercury in 10 ml of ethyl alcohol. The alcohol was evaporated, and the obtained precipitate, being a mixture of diphenylmercury and bis(trinitropropyl)mercury, was separated by recrystallization from chloroform, in which the diphenylmercury is readily soluble. Bis(trinitropropyl)mercury has m. p. 155° (from chloroform); yield 1.05 g (80.5% of theory). Evaporation of the filtrate gave 0.65 g (78% of theory) of diphenylmercury with m. p. 125° (from a 1:1 mixture of acetone and water). Literature data for diphenylmercury [7]; m. p. 125°.

Reaction of 1,1,1-trinitro-3-(trinitromethylmercuri)propane with ethylene. A stream of ethylene was passed for 10 hr into a solution of 10 g of 1,1,1-trinitro-3-(trinitromethylmercuri)propane in 50 ml of ethyl alcohol. The obtained precipitate of bis(trinitropropyl)mercury was filtered; the filtrate was evaporated to a volume of 10 ml, and here an additional amount of bis(trinitropropyl)mercury was obtained; total yield 6.9 g (65.5% of theory).

Reaction of mercury salt of trinitromethane with propylene in aqueous medium. A stream of propylene was passed for 4 hr at room temperature into 40 ml of a water solution of 10 g of the mercury salt of trinitromethane. A white crystalline precipitate of 1,1,1-trinitro-2-methyl-3-(trinitromethylmercuri)propane began to deposit within 15-20 min. The reaction mixture was allowed to stand overnight. The obtained precipitate was filtered, washed with water, air-dried, and recrystallized from chloroform; m. p. 133-134° (decompn.); yield 10.6 g (97% of theory). Found: C 11.04, 11.16; H 1.17, 1.21%.  $C_5H_6N_6O_{12}Hg$ . Calculated: C 11.06; H 1.11%.

Reaction of the above compound with bromine in chloroform solution gave 1,1,1-trinitro-2-methyl-3-(bromomercuri)propane in 86% yield, m. p. 117-118° (from chloroform). Found: Br 16.74, 16.78%.  $C_4H_6N_3O_6HgBr$ . Calculated: Br 16.93%.

1,1,1-Trinitro-2-methyl-3-(trinitromethylmercuri)propane was converted to the corresponding chloride by treatment with concd. hydrochloric acid; yield 91% of theory; m. p. 119° (from chloroform). Found: Cl 8.05, 8.11%.  $C_4H_6N_3O_6HgCl$ . Calculated: Cl 8.28%.

Reaction of mercury salt of trinitromethane with propylene in alcohol medium. A stream of propylene was passed for 5 hr into a solution of 10 g of the mercury salt of trinitromethane in 30 ml of ethyl alcohol. The solvent was evaporated to a residue of 10-12 ml and the obtained crystals of bis(1,1,1-trinitro-2-methylpropyl)mercury were filtered, washed with water, dried, and recrystallized from chloroform; m. p. 124-125° (decompn.); yield 9.25 g (79% of theory). Found: C 16.62, 16.69; H 2.19, 2.23; N 14.15, 14.21%.  $C_8H_8N_6O_{12}Hg$ . Calculated: C 16.42; H 2.06; N 14.38%.

Reaction of mercury salt of trinitromethane with styrene. With stirring, 1.2 ml (1 g; 0.01 mole) of freshly distilled styrene was added at room temperature to a solution of 5 g (0.01 mole) of the mercury salt of trinitromethane in 20 ml of water. The reaction mixture became cloudy and after several minutes a viscous colorless oil began to separate, which crystallized in 5-6 hr. The flask contents were allowed to stand overnight; the next day the 1,1,1-trinitro-2-phenyl-3-(trinitromethylmercuri)propane was filtered, washed with water, air-dried, and recrystallized from a 2:1 mixture of chloroform and carbon tetrachloride; m. p. 129°; yield 4.7 g (80% of theory). Found: C 19.53, 19.72; H 1.33, 1.43%.  $C_{10}H_8N_6O_{12}Hg$ . Calculated: C 19.85; H 1.33. Reaction of the compound with bromine in chloroform solution gave 1,1,1-trinitro-2-phenyl-3-(bromomercuri)propane in 90% yield; m. p. 135° (from chloroform). Found: Br 14.75, 14.85.  $C_9H_8N_3O_6HgBr$ . Calculated: Br 14.94%.

1,1,1-Trinitro-2-phenyl-3-(trinitromethylmercuri)propane was converted to the corresponding chloride in 82% yield by treatment with concd. hydrochloric acid; m. p. 147° (from chloroform). Found: Cl 6.98, 7.18%.  $C_9H_8N_3O_6HgCl$ . Calculated: Cl 7.23%.

1,1,1-Trinitro-2-phenyl-3-(chloromercuri)propane can be obtained in 61% yield by reacting equimolar amounts of trinitromethane, mercuric chloride and styrene in aqueous medium for 2 days.

Reaction of mercury salt of trinitromethane with cyclopentene. To a solution of 5 g (0.01 mole) of the mercury salt of trinitromethane in 20 ml of water was added 1 ml (0.68 g; 0.01 mole) of freshly distilled cyclopentene. The reaction mixture was shaken on a shaker at room temperature. After several minutes the solution turned cloudy, and after 2 hr a noticeable amount of two precipitates, a white crystalline product and a yellow oily substance, was formed. The reaction mixture was kept for three days with periodic shaking. The precipitates were separated and dried on porous plates. After two recrystallizations from carbon tetrachloride the white crystalline precipitate had m. p. 111-112° and is 1-trinitromethyl-2-(trinitromethylmercuri)cyclopentane; yield 0.9 g. Found: C 14.85, 14.96; H 1.40, 1.64; N 14.25, 14.41%.  $C_7H_8N_6O_{12}Hg$ . Calculated: C 14.78; H 1.42; N 14.78%. The yellow oily precipitate was dissolved in methyl alcohol and then precipitated with water. Here we obtained 3.5 g of yellowish crystals, which after recrystallization from hexane had m. p. 89-90° (decompn.) and represent bis(trinitromethylcyclopentyl)mercury. Found: C 22.57, 21.73; H 2.56, 2.63; N 13.07, 13.19%.  $C_{12}H_{16}O_6Hg$ . Calculated: C 22.64; H 2.52; N 13.19%.

1-Trinitromethyl-2-(trinitromethylmercuri)cyclopentane was converted to the corresponding bromide by treatment with bromine; m. p. 129.5° (from carbon tetrachloride); yield 80% of theory. Found: Br 15.95, 16.07%.  $C_6H_8N_3O_6HgBr$ . Calculated: Br 16.02%.

Reaction of mercury salt of trinitromethane with cyclohexene. To a solution of 5 g (0.01 mole) of the mercury salt of trinitromethane in 20 ml of water was added 0.82 g (1 ml; 0.01 mole) of cyclohexene. The reaction mixture was shaken on the shaker for 6 hr. The thus obtained 1-trinitromethyl-2-(trinitromethylmercuri)cyclohexane was filtered, washed with water, air-dried, and recrystallized from carbon tetrachloride; m. p. 95°; yield 3.2 g (55% of theory). Found: C 16.47, 16.53; H 1.70, 1.81%.  $C_8H_{10}N_6O_{12}Hg$ . Calculated: C 16.48; H 1.73%.

The above compound was converted to the corresponding bromide by treatment with bromine in chloroform solution; m. p. 144° (from carbon tetrachloride); yield 75% of theory. Found: Br 15.34, 15.38%.  $C_7H_{10}N_3O_6HgBr$ . Calculated: Br 15.58%.

The corresponding chloride, obtained by treating 1-trinitromethyl-2-(trinitromethylmercuri)cyclohexane with 6 N hydrochloric acid, had m. p. 152° (from chloroform). Found: Cl 7.43, 7.47%.  $C_7H_{10}N_3O_6HgCl$ . Calculated: Cl 7.59%.

#### SUMMARY

1. The reaction of the mercury salt of trinitromethane with olefins represents a reaction where the elements of the salt add directly to the double bond.

2. The obtained organomercury nitro compounds, containing a trinitromethyl group attached to the mercury atom, can exist in two tautomeric forms.

3. Compounds of type  $RHgC(NO_2)_3$ , the same as the mercury salt of trinitromethane itself, add to the double bond with the formation of compounds having the structure  $RHg-\overset{\overset{|}{|}}{\underset{\underset{|}{|}}{C}}-\overset{\overset{|}{|}}{\underset{\underset{|}{|}}{C}}-C(NO_2)_3$ , which are stable in the case of the symmetrical compound and undergo disproportionation in the case of the unsymmetrical molecule.

#### LITERATURE CITED

1. S. S. Novikov, T. I. Godovikova, and V. A. Tartakovskii, *Doklady Akad. Nauk SSSR* **124**, No. 4, 834 (1959).
2. S. S. Novikov, T. I. Godovikova, and V. A. Tartakovskii, *Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk* **1960**, 505.
3. S. S. Novikov, T. I. Godovikova, and V. A. Tartakovskii, *Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk* **1960**, 669.
4. S. S. Novikov, T. I. Godovikova, and V. A. Tartakovskii, *Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk* **1960**, 863.
5. L. G. Makarova and A. N. Nesmeyanov, *Synthetic Methods in the Field of Organometallic Compounds*, No. 3, Mercury [in Russian] (Izd. AN SSSR, Moscow, 1945) p. 53.
6. A. Hantzsch and K. Voigt, *Ber.* **45**, 109 (1912).
7. A. N. Nesmeyanov and E. J. Kahn, *Ber.* **62**, 1018 (1929).

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. Some or all of this periodical literature may well be available in English translation. A complete list of the cover-to-cover English translations appears at the back of this issue.

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## CHEMICAL TRANSFORMATIONS OF 1,1-DICHLOROALKANES

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In recent years a detailed study has been made of the chemical transformations of polyhalo derivatives, containing both the trichloromethyl and chloromethyl group in one molecule, and rules for their chemical behavior have been formulated [1]. It was established that the trichloromethyl group is inert toward nucleophilic reagents, whereas it undergoes changes with reagents having an electrophilic or radical character. The chloromethyl group, on the other hand, enters into the reaction of nucleophilic substitution by chlorine, in which connection nearly all of the transformations go with a high yield of the reaction products [1]. The present paper is devoted to a study of the chemical transformations of the dichloromethyl group under conditions that are comparable with the reaction conditions for the above indicated groupings.

Only isolated statements exist in the literature regarding the relative action of various reagents on dihaloalkanes. Mainly these reagents are alkaline in character, and their action is one of dehydrohalogenation. However, under certain conditions, like heating to 300° with water in an autoclave [2] or with aqueous lead oxide [3], the dichloromethyl group is capable of being converted to the carbonyl group; it is possible for the three chlorine atoms in 1,1,2-trichloroethane to be replaced by phenylthio groups [4]. A more detailed and systematic study of the lower haloalkanes was made by Petrenko-Kritchenko and Orotzkii [5]; they studied the reaction rates of various halo compounds with different basic reagents like KOH, Ba(OH)<sub>2</sub>, TiOH, C<sub>2</sub>H<sub>5</sub>ONa, NH<sub>3</sub>, AgNO<sub>3</sub>, etc., and established that the dihaloalkanes, containing two halogen atoms on one carbon atom, are quite unreactive compounds.

As the starting compounds, containing the dichloromethyl group, we selected 1,1-dichloroheptane, which is obtained quite easily by reacting enanthol with PCl<sub>5</sub>. As the reagents of nucleophilic character we selected C<sub>2</sub>H<sub>5</sub>ONa, NH<sub>3</sub>, NaI and C<sub>6</sub>H<sub>5</sub>SNa, and established that under the studied conditions the dichloride reacts with the sodium thiophenolate and sodium alcoholate, giving in the latter case mainly 1-chloro-1-heptene and a small amount of 1-heptyne as impurity. Long heating of the dichloride with anhydrous NaI in acetone (20 hr), or heating with NH<sub>3</sub> in alcohol at 160-170° for 6-7 hr, gave negative results; in these experiments the dichloride was recovered unchanged. Reaction of the dichloroheptane with sodium thiophenolate gave two substitution products - 1,1-di(phenylthio)heptane and, probably 1-phenylthio-1-heptene. The structure of the 1,1-di(phenylthio)heptane was proved by counter synthesis from the ethyl acetal of enanthol and thiophenol [6]. The mixed melting point of the disulfones, obtained by the oxidation of the two disulfides, was not depressed. The structure of the other product, obtained in small yield, was not proved. The dichloromethyl group proved to be more inert toward the action of electrophilic reagents than the trichloromethyl group. Attempts were made to hydrolyze 1,1-dichloroheptane with concd. H<sub>2</sub>SO<sub>4</sub>, oleum, and anhydrous nitric acid. However, neither reaction with oleum nor with sulfuric acid led to obtaining the aldehyde. Hydrolysis with nitric acid led to the isolation of an acid fraction in low yield, which, from its constants, corresponded to enanthic acid. Small amounts of anhydrous FeCl<sub>3</sub>, SbCl<sub>5</sub>, or AlCl<sub>3</sub> had hardly any dehydrochlorination effect on 1,1-dichloroheptane when heated to 80-100° (a small amount of tar is formed); the use of a large amount of AlCl<sub>3</sub> caused a brisk evolution of hydrogen chloride even in the cold, but an individual dehydrochlorination product could not be isolated. Replacement of the chlorine atoms by bromine could not be effected by treating 1,1-dichloroheptane with hydrogen bromide in the presence of AlCl<sub>3</sub>; the starting product was recovered.

The condensation of 1,1-dichloroheptane with benzene in the presence of AlCl<sub>3</sub> has been described in [7], but the author failed to determine the constants of the reaction products. A study of this reaction revealed that large amounts of AlCl<sub>3</sub> are not needed to make the reaction go; it also proved that depending on the condensation conditions used, and mainly on the temperature, it is possible to obtain either the mono- or the diphenylheptane as the principal product. Raising the temperature increases the yield of 1,1-diphenylheptane. The structure of the 1,1-diphenylheptane was proved by its oxidation to benzophenone. The formation of phenylheptane in this reaction is

not expected, since anomalous hydrogenation-dehydrogenation reactions under the influence of  $\text{AlCl}_3$  are frequently observed in the alkylation of the aromatic ring [8]. From the literature it is known that heptene is formed when 1,1-dichloroheptane is reacted with sodium in the absence of a solvent [9] or in cumene [10]. However, we found that this reaction with sodium is more complex and that 1-heptyne is also formed here, which was identified by preparing silver acetylide using the method described by Hill [11]. 1,1-Dichloroheptene is not hydrogenated under the conditions where the trichloromethyl group is easily reduced, i.e., at room temperature, a hydrogen pressure of 100-150 atm, in the presence of pyridine, and using skeletal nickel catalyst.

## EXPERIMENTAL

**Reaction of sodium ethylate with 1,1-dichloroheptane.** To the sodium ethylate, prepared from 11 g of Na in 130 ml of absolute alcohol, was added, with stirring, 34 g of 1,1-dichloroheptane, and the reaction mixture was refluxed for 10 hr. The reaction mixture was then diluted with water, and the oil was extracted with ether. The ether extract was dried over  $\text{Na}_2\text{SO}_4$ . The ether and traces of alcohol and acetylenic hydrocarbon were removed by distillation through a long column. The residue was vacuum-distilled. We obtained 16.2 g (60% of theory) of 1-chloro-1-heptene, which after redistillation had the constants: b. p. 82.5-83.5 (82 mm);  $n_D^{20}$  1.4380;  $d_4^{20}$  0.8948; found MR 38.89; calculated MR 38.92. Literature data [12]: b. p. 60-62° (61 mm);  $n_D^{20}$  1.4333. The fraction, containing the acetylenic hydrocarbon, was brominated. The liquid bromination product was vacuum-distilled; b. p. 102-112° (26 mm);  $n_D^{20}$  1.5080;  $d_4^{20}$  1.5310; weight 4.0 g; found MR 49.84.  $\text{C}_7\text{H}_{12}\text{Br}_2$ . Calculated MR 49.59.

**Chlorination of 1-chloro-1-heptene.** Chlorine was passed into a solution of 8.1 g of the chloroheptene in 50 ml of  $\text{CCl}_4$ , containing 0.2 g of anhydrous  $\text{FeCl}_3$ , and then the solution was poured into water, washed with alkali, dried, and distilled. We obtained 7.5 g of a fraction with b. p. 68-71° (3 mm), which after redistillation gave 6.0 g of 1,1,2-trichloroheptane (50% of theory) with b. p. 74° (4 mm);  $n_D^{20}$  1.4690;  $d_4^{20}$  1.1560; found MR 49.03; calculated MR 49.13. Found: C 40.87, 41.04; H 5.97, 6.14%.  $\text{C}_7\text{H}_{13}\text{Cl}_3$ . Calculated: C 41.30; H 6.44%.

**Reaction of sodium thiophenolate with 1,1-dichloroheptane.** To the sodium thiophenolate, obtained from 36 g of thiophenol and 7.5 g of metallic sodium in 150 ml of absolute alcohol, was added 20.5 g of the dichloride, and the reaction mixture was heated under reflux for 20 hr, after which it was diluted with water, and the obtained oil was extracted with chloroform. The chloroform was removed by distillation and the residue was vacuum-distilled. We obtained: fraction I, 63-80° (8 mm); 1.1 g;  $n_D^{20}$  1.4870; fraction II, 129-165° (2 mm); 3.6 g;  $n_D^{20}$  1.5540; fraction III, 170-195° (2 mm); 24.9 g;  $n_D^{20}$  1.5898. Redistillation of fraction II gave 1.3 g (5% of theory) of phenylthioheptene with b. p. 117-118° (2 mm);  $n_D^{20}$  1.5491;  $d_4^{20}$  0.9862; found MR 66.56; calculated MR 66.72. Found: C 74.08, 73.91; H 8.62, 8.61; S 15.35, 15.48%.  $\text{C}_{13}\text{H}_{18}\text{S}$ . Calculated: C 75.68; H 8.79; S 15.53%. Oxidation of the monosulfide with hydrogen peroxide in acetic acid gave a liquid sulfone with b. p. 159° (1 mm);  $n_D^{20}$  1.5298;  $d_4^{20}$  1.1030; found MR 66.73; calculated MR 67.04. Found: C 65.07, 65.14; H 7.68, 7.67; S 13.36, 13.32%.  $\text{C}_{13}\text{H}_{16}\text{O}_2\text{S}$ . Calculated: C 65.51; H 7.61; S 13.45%. Reaction of the monosulfide with 2,4-dinitrophenylhydrazine gave the hydrazone, m. p. 181-182° (from acetic acid). Found: C 46.31, 46.05; H 3.76, 3.94; N 22.31, 22.52%.  $\text{C}_{19}\text{H}_{20}\text{N}_4\text{O}_8$ . Calculated: C 46.74; H 4.12; N 22.94%. Redistillation of fraction III gave 19.4 g (50.5% of theory) of 1,1-di(phenylthio)heptane with b. p. 186-190° (2 mm);  $n_D^{20}$  1.5869;  $d_4^{20}$  1.0664; found MR 99.72; calculated MR 99.86. Found: C 72.33, 72.26; H 7.56, 7.54; S 20.39, 20.15%.  $\text{C}_{19}\text{H}_{24}\text{S}_2$ . Calculated: C 72.09; H 7.64; S 20.26%. Oxidation of the disulfide with hydrogen peroxide in acetic acid solution gave the disulfone; m. p. 92° (from alcohol). Found: C 60.19, 60.21; H 6.35, 6.36; S 17.25, 17.03%.  $\text{C}_{19}\text{H}_{20}\text{O}_4\text{S}_2$ . Calculated: C 59.97; H 6.36; S 16.85%. The 1,1-di(phenylthio)heptane, obtained from 10 g of enanthol ethyl acetal and thiophenol, had the constants:  $n_D^{20}$  1.5870;  $d_4^{20}$  1.0605, and on oxidation with  $\text{H}_2\text{O}_2$  gave the disulfone with m. p. 92-93°. The mixed melting point of the two sulfones was not depressed.

**Action of anhydrous nitric acid on 1,1-dichloroheptane.** A mixture of 19.5 g of the dichloride, purified by previous heating with concd.  $\text{HNO}_3$  for 2.5 hr at 75-80°, and 25 ml of  $\text{HNO}_3$  ( $d$  1.52) was heated for 3 hr at 70-75°. Fractional distillation of the neutral fraction gave 14.5 g of recovered dichloride with  $n_D^{20}$  1.4445. From the acid fraction we isolated 0.6 g of enanthic acid with b. p. 86-90° (3 mm);  $n_D^{20}$  1.4270, and 0.6 g of a product with b. p. 90-120° (3 mm) and  $n_D^{20}$  1.4375, which gave a positive test for chlorine (probably, chlorinated enanthic acid). Literature data for enanthic acid [13]: b. p. 86° (2 mm);  $n_D^{20}$  1.4250.

**Condensation of 1,1-dichloroheptane with benzene.** Thirty-four grams of the dichloride was added in drops to a suspension of 4 g of  $\text{AlCl}_3$  in 200 ml of dry benzene. After all of the dichloride had been added the reaction mixture was heated to 50°, where a vigorous evolution of HCl began; at the end the reaction mixture was heated for 2 hr.

After the usual workup and distillation in vacuo we obtained: fraction I, 85-90° (2 mm); 5.9 g;  $n_D^{20}$  1.5010; fraction II, 104-144° (2 mm); 4.1 g;  $n_D^{20}$  1.5190; fraction III, 145-150° (2 mm); 17.9 g;  $n_D^{20}$  1.5440; residue 8.5 g. Fraction III was 1,1-diphenylheptane (yield 35% of theory) and after redistillation had the constants: b. p. 145-146° (2 mm);  $n_D^{20}$  1.5409;  $d_4^{20}$  0.9533; found MR 83.18; calculated MR 82.74. Found: C 90.48, 90.41; H 9.43, 9.56%.  $C_{19}H_{24}$ . Calculated: C 90.41; H 9.59%. Literature data [14]: b. p. 132-134° (1 mm);  $n_D^{20}$  1.5466.

The structure of the 1,1-diphenylheptane was proved by its oxidation with chromic anhydride to benzophenone. The mixed melting point of the 2,4-dinitrophenylhydrazone of the benzophenone, obtained from the oxidation, and the authentic material was not depressed. From fraction I we isolated phenylheptane with b. p. 107° (10 mm);  $n_D^{20}$  1.4940;  $d_4^{20}$  0.8756; found MR 58.61; calculated MR 58.63. Found: C 89.03, 89.03; H 11.31, 11.21%.  $C_{13}H_{20}$ . Calculated: C 88.56; H 11.44%. Literature data for 1-phenylheptane: b. p. 99-100° (6 mm);  $n_D^{20}$  1.4870;  $d_4^{20}$  0.8565 [15]. If the dichloride is condensed with benzene in the cold the yield of phenylheptane is increased to 32%.

#### SUMMARY

1. The action of nucleophilic and electrophilic reagents on the dichloromethyl group was studied on the example of 1,1-dichloroheptane.
2. The dichloromethyl group is more inert toward the action of nucleophilic reagents than the chloromethyl group; only under the action of such strong nucleophiles as sodium thiophenolate could both of the chlorine atoms be replaced.
3. The dichloromethyl group, in contrast to the trichloromethyl group, is inert toward the action of such electrophilic reagents as concd. sulfuric and anhydrous nitric acids. However, compounds containing the dichloromethyl group are capable of condensing with benzene in the presence of aluminum chloride.

#### LITERATURE CITED

1. A. N. Nesmeyanov, R. Kh. Freidlina, and L. I. Zakharkin, *Uspekhi Khim.* **25**, 665 (1956).
2. L. Schmerling, *J. Am. Chem. Soc.* **67**, 1441 (1945); U. S. Patent 2,481,157 (1949); C. A. **44**, 651e (1950).
3. W. Spring and A. Lecrenier, *Bull. soc. chim. France* [2], **48**, 627 (1887).
4. R. Otto, *Ber.* **27**, 3055 (1894).
5. P. Petrenko-Kritchenko and V. Orotz'kii, *Ber.* **59**, 2131 (1926).
6. E. Rothstein, *J. Chem. Soc.* **1940**, 1553.
7. V. Auger, *Bull. soc. chim. France* [2], **47**, 42 (1887).
8. I. P. Tsukervanik, *Uspekhi Khim.* **26**, 1036 (1957).
9. H. Limpricht, *Ann.* **103**, 80 (1857).
10. A. F. Dobryanskii and Aliev, *Heftyano Khim.* **9**, 229 (1925).
11. A. Hill and F. Tyson, *J. Amer. Chem. Soc.* **50**, 177 (1928).
12. L. Schmerling and J. P. West, *J. Amer. Chem. Soc.* **71**, 2015 (1949).
13. R. Kh. Freidlina and E. I. Vasil'eva, *Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk* **1958**, 35.
14. G. Cauquill, J. Rouzaud, and co-workers, *Bull. soc. chim. France* **1955**, 513.
15. I. N. Nazarov and L. B. Fisher, *Zhur. Obshchei Khim.* **20**, 1114 (1950).

All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. Some or all of this periodical literature may well be available in English translation. A complete list of the cover-to-cover English translations appears at the back of this issue.

# FLUORINE CONTAINING $\beta$ -SULTONES

## COMMUNICATION 8. $\beta$ -SULTONES AS PROMOTERS OF ACYLATION

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In an earlier paper [1] the use of tetrafluoroethane- $\beta$ -sultone as a promoter for esterification of acetic acid with various alcohols was described. It could be anticipated that the promoting effect of fluorine containing  $\beta$ -sultones should apply also to the acylation of alcohols, mercaptans, and any other nucleophilic reagent with various carboxylic acids.

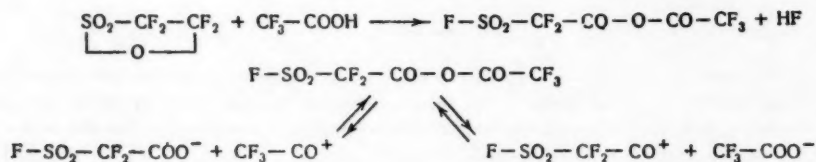
We studied the acylating effect of mixtures of tetrafluoroethane- $\beta$ -sultone and a series of aliphatic and aromatic acids, both monobasic and dibasic. It appeared that the ester was obtained in almost quantitative yield in all cases in which unsubstituted acids were used for the acylation of ethanol (Table 1). The ratio of sultone to acid in the acylation mixture was determined solely by the basicity of the latter; the ratio was 1:1 (molar) for monobasic and 1:0.5 for dibasic acids.

Completely different results were obtained with acylations carried out with mixtures of tetrafluoroethane- $\beta$ -sultone with different chloro- and fluoro-substituted acids. In all cases esters of the corresponding halogenoacetic acid and also of fluorosulfonyldifluoroacetic acid were separated (Table 2).

TABLE 1

Acid ester	Temperature of acylation, °C	Yield, %
Ethyl propionate	0	98
Ethyl isobutyrate	0	96
Diethyl oxalate	10	85
Diethyl malonate	20	78
Diethyl succinate	20	72
Ethyl benzoate	20	72
Ethyl p-toluate	20	70
Diethyl phthalate	20	67

According to the data in Table 2 the overall yield and ratio of the acylation products are dependent on the strength of the acids used in acylation. This observation confirms the earlier postulate [1] of the formation of a mixed anhydride in the mixture of sultone and carboxylic acid. This fact indicates that the ability of a mixed anhydride to dissociate into a carboxylate anion and an acyl cation depends on the difference in acid strengths of the acids taking part in its formation. Finally the relative proportions of each of the possible directions of dissociation of the mixed anhydride is determined by the relative strengths of the acids. For example in the case of the mixed anhydride of fluorosulfonyldifluoroacetic and trifluoroacetic acids (which are similar in acid strength) both possible directions of dissociation occur to the same extent in practice.



In connection with the observations cited it is appropriate to recall that attempted acylation of alcohols with a solution of monochloroacetic acid in trifluoroacetic anhydride was without result [2]. The acylating power of a mixture of tetrafluoroethane- $\beta$ -sultone and a carboxylic acid can also be demonstrated in the preparation of thioesters (Table 3).



Other  $\beta,\beta$ -fluorocontaining  $\beta$ -sultones can be used as acylation promoters. Thus the reaction mixtures formed from a mixture of a carboxylic acid with  $\alpha$ -hydrotrifluoroethane- or perfluoroisopropane- $\beta$ -sultone are effective acylating reagents (Table 4).

TABLE 2

Acid	Yield, %				Ratio
	R-CO-OCH <sub>3</sub>	FSO <sub>2</sub> -CF <sub>2</sub> -CO-OCH <sub>3</sub>	overall		
Chloroacetic	70	22	92		3.18
Fluoroacetic	59	31	90		1.91
Difluoroacetic	49	35	84		1.40
Trifluoroacetic	36	35	71		1.03

TABLE 3

Acid thioester	Acylation temperature, °C	Yield, %
Ethyl thioacetate	20	80
n-Propyl thioacetate	20	83
n-Butyl thioacetate	20	88
$\beta$ -Chloroethyl thioacetate	10	85
Ethyl thiobenzoate	30	71

TABLE 4

Sultone	Acid ester	Yield, %
$\alpha$ -Hydrotrifluoroethane- $\beta$ -sultone	Ethyl acetate	99
" " " "	$\beta$ -Chloroethyl acetate	86
" " " "	Phenyl acetate	70
" " " "	Ethyl propionate	97
" " " "	Ethyl benzoate	75
" " " "	Ethyl thioacetate	78
$\alpha$ -Chlorotrifluoroethane- $\beta$ -sultone	Ethyl acetate	97
" " " "	Ethyl benzoate	72
Perfluoroisopropane- $\beta$ -sultone	Ethyl acetate	98
" " " "	Ethyl benzoate	75

Thus the promoting effect of fluorine containing  $\beta$ -sultones relative to acylation is comparatively widespread and should be displayed when  $\beta$ -sultones are used as an acylating medium with weak heteroorganic and mineral acids.

#### EXPERIMENTAL

**Acylation of alcohols and mercaptans.** To 0.1 M fluorine containing  $\beta$ -sultone in a teflon reactor, 0.1 M of the corresponding monobasic or 0.05 M of dibasic acid was added in small portions with stirring and ice-cooling. Then at a temperature of from 0-20° (see Tables 1 and 3) 0.1 M absolute alcohol or mercaptan was added. The reaction mixture was poured into a cooled solution of 10 g potassium fluoride in 30 ml water. The oily layer was separated, dried over magnesium sulfate, and fractionated.

#### SUMMARY

1. Fluorine containing  $\beta$ -sultones are promoters of the acylation of alcohols and mercaptans by weak carboxylic acids.
2. The acylating properties of mixtures of tetrafluoroethane- $\beta$ -sultone with halogen substituted carboxylic acids have been studied.

#### LITERATURE CITED

1. G. A. Solol'skii and I. L. Knunyants, *Izv. AN SSSR, Otd. Khim. Nauk* 1961, No. 5.
2. J. M. Tedder, *Chem. Revs.* 55, 787 (1955).

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# FLUORINE CONTAINING $\beta$ -SULTONES

## COMMUNICATION 9. REACTION OF FLUORINE CONTAINING $\beta$ -SULTONES WITH MERCAPTANS

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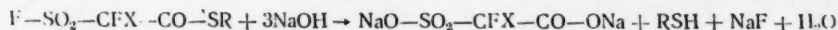
Original article submitted June 4, 1960

It was earlier reported that fluorine containing  $\beta$ -sultones reacted energetically with compounds containing active hydrogen atoms and in particular on reaction with alcohols, esters of substituted  $\beta$ -fluorosulfonylcarboxylic acids were obtained. In the present communication the reaction of fluorine containing  $\beta$ -sultones with mercaptans is described. This reaction was investigated for the interactions of tetrafluoroethane- $\beta$ -sultone,  $\alpha$ -hydrotrifluoroethane- $\beta$ -sultone, and  $\alpha$ -chlorotrifluoroethane- $\beta$ -sultone with n-propyl, n-butyl and  $\beta$ -chloroethyl mercaptans. In all cases the reaction was carried out by gradual addition of one reactant to the other; it was accompanied by considerable self-heating of the reaction mixture and evolution of hydrogen fluoride. It is interesting to note that the character of the reaction is connected with the structure of the original  $\beta$ -sultone. Thus in the case of tetrafluoroethane- $\beta$ -sultone the reaction proceeds so vigorously that tar formation may occur in the reaction mixture; to prevent tar formation it is necessary to use considerable cooling. With  $\alpha$ -hydrotrifluoroethane- $\beta$ -sultone the reaction goes with less evolution of heat, but with  $\alpha$ -chlorotrifluoroethane- $\beta$ -sultone it is necessary to heat the reaction mixture (to 20-30°) to initiate reaction.

In all cases the products of the reaction between fluorine containing  $\beta$ -sultones and mercaptans are the corresponding thioesters of substituted fluorosulfonylacetic acids



The yield of the thioester depends on the order of mixing of the reagents. Thus when the mercaptan was added to the  $\beta$ -sultone the yield of thioester did not exceed 35-42%. With reversed order of mixing of the reagents the yield of thioester reached 70-80%. This observation can be explained by the fact that in the first case there is an excess of  $\beta$ -sultone during the mixing process, and the  $\beta$ -sultone possesses a high oxidation potential because of the sulfur trioxide group, and is capable of oxidizing the sulfhydryl group of the mercaptan. When an excess of mercaptan is present during the mixing, the oxidation reaction does not prevail and the thioester is formed in high yield. The thioesters of substituted fluorosulfonylacetic acids formed are stable colorless liquids with a specific sulfide smell; they dissolve well in organic solvents but to a very limited extent in water. The thioesters undergo noticeable hydrolysis only after standing for many hours in dilute aqueous solution. The thioesters are hydrolyzed practically instantaneously by aqueous alkali and the dibasic salts of substituted sulfonylacetic acids are formed quantitatively and the mercaptans separate.



### EXPERIMENTAL

Butyl fluorosulfonyldifluorothioacetate. 9.0 g tetrafluoroethane- $\beta$ -sultone was added slowly to 4.5 g n-butyl mercaptan with shaking and cooling in iced water. The mixture was observed to get warm and hydrogen fluoride was evolved. The solution became brick red. At the end of the addition the mixture was poured onto 20 g ice; the lower layer was separated, washed with 10 ml iced water, and dried over calcined magnesium sulfate. By subsequent fractionation 10.3 g n-butyl fluorosulfonyldifluorothioacetate was separated; b. p. 68° (5 mm);  $d^{20}_4$  1.3171;  $n^{20}_D$  1.4100; yield 82%. Found: C 28.18; H 3.51; F 22.44; S 25.90%; acid equivalent 2.95, iodine equivalent 0.99,  $\text{C}_6\text{H}_5\text{O}_3\text{F}_3\text{S}_2$ . Calculated: C 28.40; H 3.60; F 22.80; S 25.60%; acid equivalent 3.00; iodine equivalent 1.00.

With reversed order of mixing of the reagents n-butyl fluorosulfonyldifluorothioacetate was obtained in 35% yield.

$\beta$ -Chloroethyl fluorosulfonyldifluorothioacetate. In similar conditions  $\beta$ -chloroethyl fluorosulfonyldifluorothioacetate was obtained from  $\beta$ -chloroethylmercaptan and tetrafluoroethane- $\beta$ -sultone in 78% yield, b. p. 81° (7 mm);  $d_4^{20}$  1.5763;  $n_D^{20}$  1.4380.\* Found: F 22.70; Cl 14.03; S 25.18%.  $C_4H_4O_3F_5ClS_2$ . Calculated: F 22.42; Cl 13.83; S 24.96%.

n-Propyl fluorosulfonylfluorothioacetate. In similar conditions n-propyl fluorosulfonyldifluorothioacetate was obtained in 76% yield from n-propyl mercaptan and  $\alpha$ -hydrotrifluoroethane- $\beta$ -sultone, b. p. 114-115° (20 mm);  $d_4^{20}$  1.3456;  $n_D^{20}$  1.4355. Found: F 18.02; C 27.92; H 3.52%; acid equivalent 2.96; iodine equivalent 0.98.  $C_5H_8O_3F_2S_2$ . Calculated: F 17.64; C 27.50; H 3.67%; acid equivalent 3.00; iodine equivalent 1.00.

n-Butyl fluorosulfonylfluorothioacetate. In similar conditions n-butyl fluorosulfonylfluorothioacetate was obtained in 72% yield from n-butyl mercaptan and  $\alpha$ -hydrotrifluoroethane- $\beta$ -sultone, b. p. 127-128° (20 mm);  $d_4^{20}$  1.2895;  $n_D^{20}$  1.4355. Found: F 16.68%; acid equivalent 3.02; iodine equivalent 1.03.  $C_6H_{10}O_3F_2S_2$ . Calculated: F 16.38%; acid equivalent 3.00; iodine equivalent 1.00.

$\beta$ -Chloroethyl fluorosulfonylfluorochlorothioacetate was obtained under similar conditions (65% yield) from  $\beta$ -chloroethyl mercaptan and  $\alpha$ -hydrotrifluoroethane- $\beta$ -sultone, b. p. 117° (8 mm);  $d_4^{20}$  1.5425;  $n_D^{20}$  1.4600. Found: F 16.30; Cl 14.61; S 26.59%.  $C_4H_5O_3F_2ClS_2$ . Calculated: F 15.92; Cl 14.87; S 26.86%.

n-Butyl fluorosulfonylfluorochlorothioacetate. By the method described above n-butyl fluorosulfonylfluorochlorothioacetate was obtained in 80% yield at room temperature from n-butyl mercaptan and  $\alpha$ -chlorotrifluoroethane- $\beta$ -sultone, b. p. 80° (5 mm);  $d_4^{20}$  1.2757;  $n_D^{20}$  1.4220. Found: C 26.84; H 3.60; F 14.65; Cl 13.11%.  $C_4H_9O_3F_2ClS_2$ . Calculated: C 27.04; H 3.57; F 14.25; Cl 13.32%.

$\beta$ -Chloroethyl fluorosulfonylfluorochlorothioacetate was obtained in 75% yield under similar conditions from  $\beta$ -chloroethyl mercaptan and  $\alpha$ -chlorotrifluoroethane- $\beta$ -sultone, b. p. 86° (4 mm);  $d_4^{20}$  1.4557;  $n_D^{20}$  1.4560. Found: F 14.30; Cl 25.74%.  $C_4H_4O_3F_2Cl_2S_2$ . Calculated: F 13.92; Cl 26.00%.

#### SUMMARY

The reaction between fluorine containing  $\beta$ -sultones and mercaptans has been studied and a series of thioesters of substituted fluorosulfonylacetic acids has been obtained.

#### LITERATURE CITED

1. M. A. Dmitriev, G. A. Sokol'skii, and I. L. Knunyants, Doklady Akad. Nauk SSSR 124, 581 (1959).

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. Some or all of this periodical literature may well be available in English translation. A complete list of the cover-to-cover English translations appears at the back of this issue.

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\*The physical constants of this thioester recorded in a preceeding communication [1] are inexact because of an error in transcription by the experimenter.



# UNSATURATED ACIDS CONTAINING A TRIFLUOROMETHYL GROUP

## COMMUNICATION 3. POLARIZATION OF THE DOUBLE BOND IN $\beta$ -TRIFLUOROMETHYLCROTONIC ACID

I. L. Knunyants and Yu. A. Cheburkov

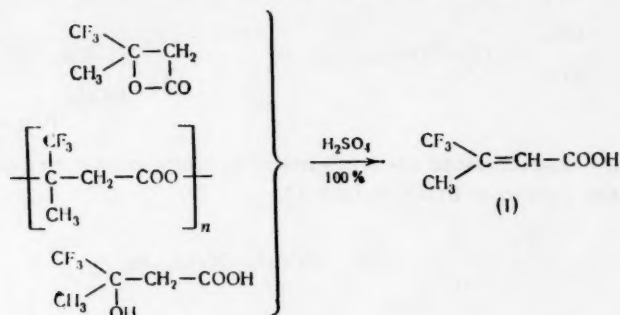
Institute of Heteroorganic Compounds, Academy of Sciences of the USSR

Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*,

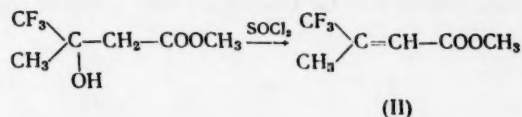
No. 6, pp. 1057-1062, June, 1961

Original article submitted March 21, 1960

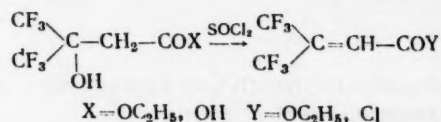
$\beta$ -Trifluoromethylcrotonic acid (I) was first obtained in 1955 by dehydration of  $\beta$ -trifluoromethyl- $\beta$ -hydroxybutyric acid with phosphorus pentoxide. Investigations showed that this acid was easily prepared by dissolving  $\beta$ -trifluoromethyl- $\beta$ -methyl- $\beta$ -propiolactone, its polymer, or  $\beta$ -trifluoromethyl- $\beta$ -hydroxybutyric acid in anhydrous (but not 96%) sulphuric acid:



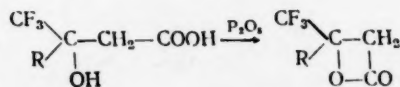
The peculiar specificity of 100% sulfuric acid relative to  $\beta$ -hydroxy acids containing trifluoromethyl groups in the  $\beta$ -position was discussed earlier [2]. Methyl  $\beta$ -trifluoromethylcrotonate (II) can be obtained by dehydration of the corresponding ester of the  $\beta$ -hydroxy acid with thionyl chloride:

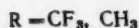
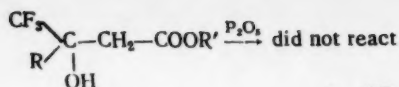


As was found earlier thionyl chloride also easily dehydrates  $\beta,\beta$ -bistrifluoromethyl- $\beta$ -hydroxypropionic acid and its ester to give the acid chloride and ester respectively of the unsaturated acid [3].

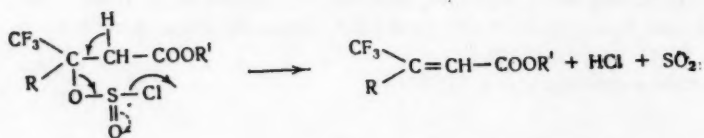


At the same time dehydration with phosphorus pentoxide of a  $\beta$ -hydroxy acid containing fluorine gives the corresponding  $\beta$ -lactone [2, 4], whereas the esters of these acids are not dehydrated at all by phosphorus pentoxide [5]

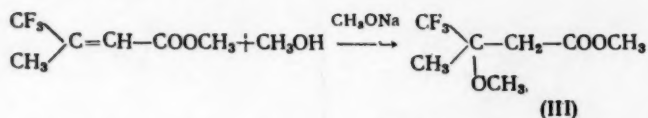




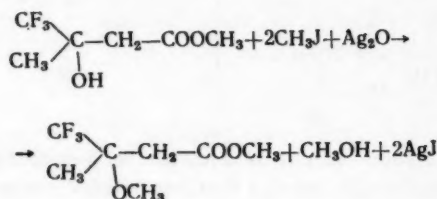
Such differences in dehydrating power of phosphorus pentoxide and thionyl chloride may be explained by weakening of the link between the tertiary carbon and the hydroxy group in the intermediate reaction product formed by reaction with thionyl chloride consequent upon the possibility of elimination of a chloride atom with a pair of electrons:



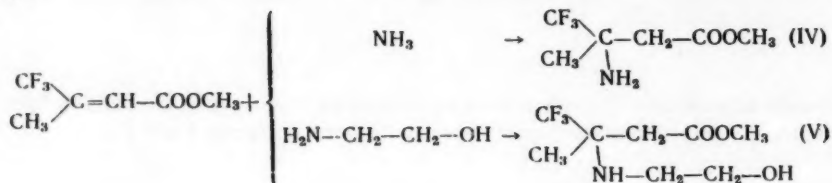
The effect of nucleophiles on  $\beta$ -trifluoromethylcrotonic acid and its ester was studied for the addition of methanol, ammonia, ethanolamine and water. Methanol in the presence of sodium methoxide added to methyl  $\beta$ -trifluoromethylcrotonate to give methyl  $\beta$ -methoxy- $\beta$ -trifluoromethylbutyrate (III).



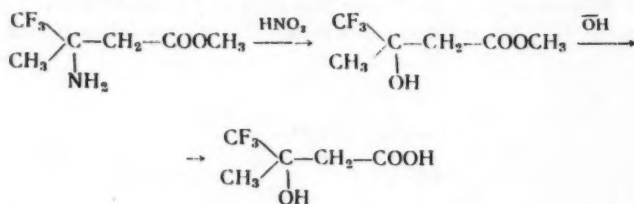
The structure of the product obtained was demonstrated by synthesizing it by methylation of  $\beta$ -trifluoromethyl- $\beta$ -hydroxybutyric acid using Purdie and Irvin's method [6].



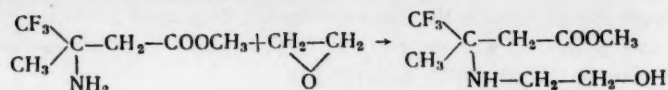
Ammonia and ethanolamine reacted with the unsaturated ester II to give esters of the corresponding aminoacids (IV) and (V).



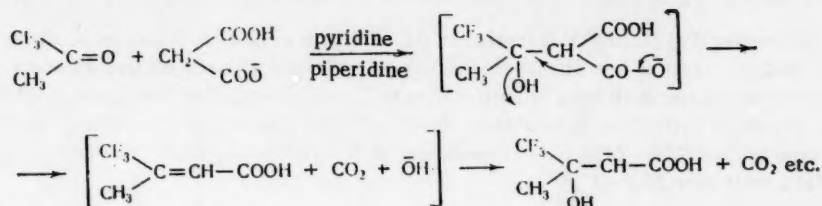
Methyl  $\beta$ -trifluoromethyl- $\beta$ -amino butyrate (IV), on treatment with nitrous acid and subsequent alkaline hydrolysis gave the known  $\beta$ -trifluoromethyl- $\beta$ -hydroxybutyric acid.



The structure of methyl  $\beta$ -trifluoromethyl- $\beta$ -(N- $\beta$ -hydroxyethyl)-aminobutyrate was demonstrated by an opposing synthesis from the amino ester (IV) and ethylene oxide.



Water does not add to  $\beta$ -trifluoromethylcrotonic acid on heating to 150° in the presence of strong bases or mineral acids, nor in pyridine solution in the presence of piperidine. However hydration of  $\beta$ -trifluoromethylcrotonic acid was postulated as one stage in the mechanism of the reaction of trifluoroacetone with malonic acid [1].



Evidently this mechanism needs reexamination.

## EXPERIMENTAL

**$\beta$ -Trifluoromethylcrotonic acid.** A mixture of 1.06 g  $\beta$ -trifluoromethyl- $\beta$ -methyl- $\beta$ -propiolactone and 1 ml 100% sulphuric acid was left standing for 1 hr, then diluted with water. The acid (I) was steam distilled - it crystallized in the receiver. After drying 0.97 g (91%) of crystals were obtained with m.p. 29.5-31°, b.p. ~182°. Literature data [1] b.p. 80-84°. Found: C 38.67; H 3.25; F 37.18%.  $\text{C}_5\text{F}_3\text{H}_5\text{O}_2$ . Calculated: C 38.98; H 3.25; F 37.00%.

A mixture of 1.25 g  $\beta$ -trifluoromethyl- $\beta$ -hydroxybutyric acid and 5 ml (1%) oleum was kept for 12 hr, and then worked up as in the previous experiment. 0.98 g (87%) of acid (I) was obtained.

By similar treatment of 4.2 g of the polymer obtained from  $\beta$ -trifluoromethyl- $\beta$ -methyl- $\beta$ -propiolactone the acid I was obtained in 70% yield.

**Methyl  $\beta$ -trifluoromethylcrotonate.** The ester (II) was obtained in 75% yield on esterifying the acid (I) with methanol in the presence of sulphuric acid; b. p. 112.5-113.5° (753 mm);  $n_D^{20}$  1.3718;  $d_4^{20}$  1.2074; found MR 31.61; calculated MR 31.52. Found: C 42.72; H 4.17; F 33.68%.  $\text{C}_6\text{F}_3\text{H}_7\text{O}_2$ . Calculated: C 42.84; H 4.16; F 33.92%.

A mixture of 9.43 g (0.051 M) methyl  $\beta$ -trifluoromethyl- $\beta$ -hydroxybutyrate, 6.50 g (0.055 M) thionyl chloride, and 1 ml dry pyridine were refluxed for 8 hr, and then fractionally distilled through a 400 mm column; in this way 6.0 g (71%) of the ester (II) was obtained b. p. 112.5-113° (751 mm);  $n_D^{20}$  1.3720.

**Methyl  $\beta$ -trifluoromethyl- $\beta$ -methoxybutyrate.** 16.8 g (0.1 M) of (II) and sodium methoxide (obtained from 1 g sodium and 50 ml methanol) were heated in a sealed ampoule for 16 hr at 100°. When the heating was completed the solution was diluted with water, acidified, the oil separated, taken up into ether and dried over calcium chloride. After removal of the solvent the residue was fractionated through a 400 mm column. Fractions were collected: I - b. p. 110-114°, initial ester, 1.57 g; II - b. p. 59.5-60.5° (22 mm), 7.85 g; III - residue ~ 2.5 g.

Fraction II was the pure product (III); b. p. 159° (744 mm); yield 45%, based on ester (II) consumed in the reaction;  $n_D^{20}$  1.3766;  $d_4^{20}$  1.230; found MR 37.36; calculated MR 38.25. Found: C 42.36; H 5.43; F 28.45%.  $\text{C}_7\text{F}_3\text{H}_{11}\text{O}_3$ . Calculated: C 42.00; H 5.54; F 28.50%.

A mixture of 12.66 g (0.068 M) methyl  $\beta$ -trifluoromethyl- $\beta$ -hydroxybutyric acid, 23.2 g (0.1 M) dry silver oxide, and 40 ml methyl iodide was boiled in a flask under reflux for 10 hr. At the end of the reaction the precipitate was sucked out and washed with ether. The ether washings and the solution were combined, dried and distilled after removal of the solvent, 11.54 g of a colorless liquid with b. p. 158-164° (749 mm) was obtained which appeared to be a mixture of the initial hydroxyester and the methoxyester (III). Further separation of the products was carried out by treating the mixture in the cold with 30% alkali. The oil which did not dissolve in the alkali was separated,

\* It is possible that a misprint occurred in the constant cited.

taken up in ether and distilled after drying and removing the solvent. 1.8 g (III) (57% based on hydroxyester consumed in the reaction) was obtained with b. p. 158.5-160.5° (749 mm);  $n_D^{20}$  1.3769. The product obtained was identical in its properties with that obtained in the first experiment. Thus it did not dissolve in 30% alkali in the cold and it did not react with sodium in ether with the evolution of hydrogen, which distinguished it from methyl  $\beta$ -trifluoromethyl- $\beta$ -hydroxybutyrate which has similar constants [7].

Methyl  $\beta$ -trifluoromethyl- $\beta$ -aminobutyrate. A mixture of 7.5 g of the ester (II) and a fivefold excess of dry ammonia were kept in a sealed ampoule for 48 hr at room temperature. The excess ammonia was evaporated and the residue distilled in vacuum to give 7.3 g (89%) of the aminoester (IV), b. p. 93.5 (73 mm);  $n_D^{20}$  1.3842;  $d_4^{20}$  1.2501; found MR 34.61; calculated MR 35.40. Found: C 38.99; H 5.45; F 30.26; N 8.02%.  $C_6F_3H_{10}O_2N$ . Calculated: C 38.92; H 5.42; F 30.82; N 7.56%. The hydrochloride was soluble in water, m. p. 128-129.5° (from ethyl acetate).

The aminoester (IV) (1.35 g) was treated in the cold with a solution of sodium nitrite in the presence of sulphuric acid until an excess of free nitrous acid remained. The precipitated oil was washed with water and heated with 20% alkali on a water bath for 1 hr until it dissolved completely. The solution was acidified and extracted with ether. The ether extracts were combined, dried, and after removal of the solvent, the residue was recrystallized from n-heptane to give 0.56 g (45%)  $\beta$ -trifluoroethyl- $\beta$ -hydroxybutyric acid. The melting points of the samples and of a mixed melt were 39.5-41°.

Methyl  $\beta$ -trifluoromethyl- $\beta$ -(N- $\beta$ -hydroxyethyl) aminobutyrate. 7.23 g (0.043 M) of the ester (II) and 2.64 g (0.043 M) ethanalamine were heated at 80° for 5 hr in a sealed ampoule. On another day the reaction mixture was distilled in vacuum.

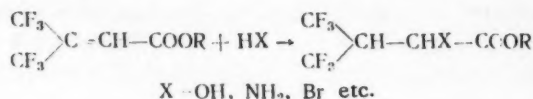
The ester (V) was obtained in 40% yield (3.91 g); b. p. 138.5-141° (18 mm);  $n_D^{20}$  1.4165;  $d_4^{20}$  1.2649; found MR 45.47; calculated MR 46.35; the hydrochloride has m. p. 101-103° (reprecipitated with absolute ether from absolute ethanol). Found: C 36.06; H 5.62; F 20.47; N 5.33%.  $C_8F_3H_{15}O_3NCl$ . Calculated: C 36.15; H 5.65; F 21.46; N 5.27%.

A fraction (3.15g) with b. p. 160-163° (7 mm),  $n_D^{20}$  1.4400 was also obtained. It did not dissolve in dilute hydrochloric acid. This fraction was not studied further.

A mixture of 4.6 g (0.025 M) of the ester (IV), 1.25 g (0.028 M) ethylene oxide, and 25 ml 50% acetic acid was kept at room temperature for 12 hr; the solution was then neutralized with dry soda, the oil separated, taken up in ether and dried over magnesium sulfate. After evaporation of the ether and distillation in vacuum, 2.27 g of the initial aminoester (IV) was obtained [b. p. 65-66° (72 mm);  $n_D^{20}$  1.3873 (hydrochloride gave no depression of the melting point with an authentic sample)] together with 1.47 g of the ester V;  $n_D^{20}$  1.4152 (hydrochloride gave no depression of the melting point with a sample from the first experiment). The yield was 51%, calculated on the aminoester (IV) consumed in the reaction.

## Discussion of Experimental Results

In previous papers of this series it was shown that water, hydrogen bromide, ammonia, and other substances added to  $\beta,\beta$ -bistrifluoromethylacrylic acid and its esters in the  $\alpha$ -position to the carboxyl group [3, 8, 9]:

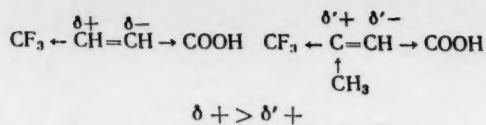


Such a direction of addition has not been observed previously in other  $\alpha, \beta$ -saturated acids. This may be explained either by the electronic effect of the trifluoromethyl group or by steric hindrance to addition of the groups in the  $\beta$ -position.

To estimate the relative importance of these two factors it was of interest to study additions to  $\beta$ -trifluoromethylcrotonic acid in which steric hindrance at the  $\beta$ -carbon atom ought to be about the same as in  $\beta,\beta$ -bistrifluoromethylacrylic acid because of the small difference in volume of the trifluoromethyl and methyl groups.

At the same time the polarization of the double bond in this acid ought to be the same as in  $\gamma,\gamma,\gamma$ -trifluorocrotonic acid in which the effect of the trifluoromethyl group is not weakened by the neighboring methyl which nevertheless appears insufficient to draw away the  $\pi$ -electrons from the  $\alpha$ -carbon atom [10]:





With this polarization the presence of steric hindrance should lead to considerable hindrance or complete impossibility of addition to  $\beta$ -trifluoromethylcrotonic acid.

As our investigations have shown, additions of nucleophilic reagents to  $\beta$ -trifluoromethylcrotonic acid proceed in mild conditions and in accordance with the anticipated polarization of the double bond. Hence it can be concluded that in the case of  $\beta,\beta$ -trifluoromethylacrylic steric hindrance plays a subordinate part in determining the direction of addition.

#### SUMMARY

1.  $\beta$ -Trifluoromethylcrotonic acid was obtained by the action of anhydrous sulfuric acid on  $\beta$ -trifluoromethyl- $\beta$ -methylpropiolactone or  $\beta$ -trifluoromethyl- $\beta$ -hydroxybutyric acid.
2. Thionyl chloride in distinction from phosphorus pentoxide easily dehydrates methyl  $\beta$ -trifluoromethyl- $\beta$ -hydroxybutyrate.
3. After studying the direction of addition of methanol, ammonia, and ethanolamine to esters of  $\beta$ -trifluoromethylcrotonic acid it was concluded that the deciding role in the addition of nucleophilic reagents was played by polarization of the double bond, not steric hindrance.

#### LITERATURE CITED

1. H. Walborsky, M. Baum, and D. Loncrini, J. Amer. Chem. Soc. **77**, 3637 (1955).
2. I. L. Knunyants and Yu. A. Cheburkov, Izv. AN SSSR, Otd. Khim. Nauk **1960**, 678.
3. I. L. Knunyants and Yu. A. Cheburkov, Izv. AN SSSR, Otd. Khim. Nauk **1960**, 2168.
4. I. L. Knunyants and Yu. A. Cheburkov, Izv. AN SSSR, Otd. Khim. Nauk **1961**, No. 5.
5. I. L. Knunyants, N. P. Gambaryan, and Cheng Ching-yün, Izv. AN SSSR, Otd. Khim. Nauk **1960**, 686.
6. T. Purdie and J. Irvin, J. Chem. Soc. **75**, 483 (1899).
7. I. L. Knunyants and Yu. A. Cheburkov, Izv. AN SSSR, Otd. Khim. Nauk **1961**, No. 5.
8. I. L. Knunyants and Yu. A. Cheburkov, Izv. AN SSSR, Otd. Khim. Nauk **1960**, 2162.
9. I. L. Knunyants and Yu. A. Cheburkov, Izv. AN SSSR, Otd. Khim. Nauk **1960**, 1516.
10. H. Walborsky and M. Schwarz, J. Amer. Chem. Soc. **75**, 3241 (1953).

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. Some or all of this periodical literature may well be available in English translation. A complete list of the cover-to-cover English translations appears at the back of this issue.

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# FLUORINATED STYRENES

## COMMUNICATION 5. $\alpha, \beta, \beta$ -TRIFLUOROSTYRENES

G. V. Kazennikova, T. V. Talalaeva, A. V. Zimin,

A. P. Simonov, and K. A. Kocheshkov

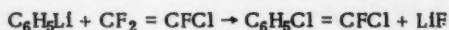
L. Ya. Karpov Physicochemical Institute

Translated from *Izvestiya Akademii Nauk SSSR, Otdeleniye Khimicheskikh Nauk*,

No. 6, pp. 1063-1065, June, 1961

Original article submitted April 1, 1960

The shortest route for the synthesis of styrenes fluorinated in the side chain is condensation of fluoroolefins with organolithium, -magnesium, and -sodium compounds. These reactions go at a temperature of about  $-75^\circ$  in ether medium. With phenyllithium and trifluorochloroethylene,  $\alpha, \beta$ -difluoro- $\beta$ -chlorostyrene [1] was obtained in 91% yield



When phenylcalcium iodide was used, the yield was 38%, with phenylmagnesium bromide it was 16.6% [2], and for triphenylmethylsodium with trifluorochloroethylene under the same conditions the yield of 1,2-difluoro-1-chloro-2-triphenylmethylethylene was 94% [1]. When 1,1-difluoro-2,2-dichloroethylene and phenyllithium were used,  $\alpha$ -fluoro- $\beta, \beta$ -dichlorostyrene  $\text{C}_6\text{H}_5\text{CF} = \text{CCl}_2$  was obtained in 50% yield [3]. Under these conditions fluorinated vinylidene and 1,2-dichloro-1,2-difluoroethylene did not react with phenyllithium or form complex mixtures of reaction products [3]. We were interested in the synthesis of  $\alpha, \beta, \beta$ -trifluorostyrenes, i.e., in the possibility of preparing these compounds by the condensation of tetrafluoroethylene with organometallic compounds of the aromatic series



In the literature the preparation of  $\alpha, \beta, \beta$ -trifluorostyrene in 30% yield by the slow addition of an ether solution of phenyllithium to an excess of tetrafluoroethylene at  $-80^\circ$  is indicated. The method is not described [3]. It is indicated that with an excess of phenyllithium the formation of difluorostilbene  $\text{C}_6\text{H}_5\text{CF} = \text{CFC}_6\text{H}_5$  takes place, and that with an increase in the reaction temperature to  $25^\circ$  triphenylfluoroethylene is produced [3]. It was not possible to replace the last atom of fluorine on the phenyl group [1].

We found that when the reaction was carried out under conditions where a solution of phenyllithium was added to the tetrafluoroethylene at  $-75^\circ$ , the yield of  $\alpha, \beta, \beta$ -trifluorostyrene amounted to 25-15%; lowering the reaction temperature to  $-120^\circ$  did not increase the yield of the styrene. It was possible to obtain  $\alpha, \beta, \beta$ -trifluorostyrene in 30-40% yield by reversing the order of addition of the components, i.e., by rapidly passing an excess of pure tetrafluoroethylene into a dilute ether solution of phenyllithium in 1-2 hr. Use of concentrated solutions of phenyllithium or increasing the time of passing the tetrafluoroethylene lowered the yield to 15-20%. Condensation of tetrafluoroethylene with organolithium compounds at low temperature proved to be a general method for the preparation of new  $\alpha, \beta, \beta$ -trifluorostyrenes and perfluorovinyl compounds. The yield in this condensation, depending on the radical of the RLi, usually amounted to 40-55%, more rarely 15-30%. The corresponding difluorostilbene was produced as a by product.

The  $\alpha, \beta, \beta$ -trifluorostyrenes prepared were monomers and could be stored for a long time sealed in ampoules under argon, over a small amount of powdered copper at a temperature from  $-25^\circ$  to  $-35^\circ$ . Formation of the dimer [4] during such storage was negligible. One distillation (in nitrogen or argon) was sufficient for purification of the monomer before polymerization.

As examples we cited the synthesis of  $\alpha, \beta, \beta$ -trifluoro-*p*-methylstyrene (40%),  $\alpha, \beta, \beta$ -trifluoro-*o*-methylstyrene (55%),  $\alpha, \beta, \beta$ -trifluoro-*m*-methylstyrene (46%). In the same way it was possible to obtain  $\alpha, \beta, \beta$ -tri-

fluoro-p-chlorostyrene (15%) and a small yield of  $\alpha, \beta, \beta$ -trifluoro-p-bromostyrene (5-10%).  $\alpha$ -Perfluorovinyl-naphthalene was prepared in about 10% yield. When tetrafluoroethylene was reacted with tetramethylenedilithium, pentamethylenedilithium, and decamethylenedilithium unsaturated compounds  $\text{CF}_2 = \text{CF}(\text{CH}_2)_n\text{CF} = \text{CF}_2$  were obtained in about 35% yield. With butyllithium, as described also in the literature [3], only one reaction product,  $n\text{-C}_4\text{H}_9\text{CF} = \text{CF}_2$ , was obtained.

In order to confirm the structure of the compounds under investigation, we obtained their IR spectra in the region from 2000 to 650  $\text{cm}^{-1}$ . Of most interest in the IR spectra of the monomers investigated was the position of

the band related to the valence vibration of the  $\text{C}=\text{C}$  group (table).

Vibrations (frequencies in $\text{cm}^{-1}$ )	$\alpha, \beta, \beta$ -Trifluorostyrene	$\alpha, \beta, \beta$ -Trifluoromethylstyrenes		
		para	meta	ortho
Valence vibration $\text{C}=\text{C}$	1765 (v.s.)	1767 (v.s.)	1767 (v.s.)	1788 (v.s.)
Valence vibration of skeleton of benzene ring	1607 (wk.) 1507 (med.)	1620 (med.) 1522 (med.)	1612 (med.) 1497 (med.)	1613 (med.) 1496 (med.)
Valence vibration of C-F	1291 (v.s.) 1196 (med.) 1158 (v.s.) 994 (s.)	1296 (v.s.) 1199 (med.) 1159 (v.s.) 995 (v.s.)	1291 (v.s.) 1201 (s.) 1146 (s.) 981 (med.)	1275 (v.s.) 1203 (med.) 1128 (v.s.) 978 (v.s.)
Nonplanar deformation vibrations of CH	— 777 (s.) — 693 (s.)	825 (s.) — 736 (med.) —	— 776 (med.) — 683 (med.)	— — 748 (s.) —

It is well known that replacement of hydrogen by fluorine at a double bond elicits a shift in the frequency of the vibration of the  $\text{C}=\text{C}$  grouping in the direction of the higher frequencies and an increase in the intensity of the absorption. This shift in the case of  $\alpha, \beta, \beta$ -trifluorostyrene is 130  $\text{cm}^{-1}$  in relation to the frequency of this vibration in styrene [5]. From the table it is seen that the methyl group in the ortho position causes a shift of the band related to the valence vibration of the  $\text{C}=\text{C}$  in the direction of higher frequencies, which indicates a strengthening of the  $\text{C}=\text{C}$  bond. This is in agreement with data on the polymerization of the compounds investigated. The position of the bands relating to the valence vibrations of the skeleton of the benzene ring and the nonplanar deformation vibrations of CH characteristic of the monosubstituted para-, meta-, and ortho-disubstituted derivatives of benzene [6] confirms the structure of the monomers investigated. In the region of the valence vibrations of C-F there is a series of bands, the most intense of which are included in the table.

#### EXPERIMENTAL

Ether solutions of the organolithium compounds were prepared under the usual conditions from the alkyl halides and lithium under nitrogen. Filtration and siphoning of the solutions were carried out under argon. The styrenes were analyzed by the method of Zimin et al. [7].

**Preparation of  $\alpha, \beta, \beta$ -trifluoro-p-methylstyrene.** In an apparatus for low temperature condensations with a capacity of 1 liter, 450 ml of an ether solution of p-tolylolithium (15.1 g; 0.15 M) was placed under argon and cooled to  $-78^\circ$ . At this temperature 45 g of pure tetrafluoroethylene (0.45 M) was passed in with vigorous stirring, over a period of 1.5 hr, the mixture was stirred for another 15 minutes, and then was decomposed by careful pouring into water and ice acidified with hydrochloric acid. After the usual treatment, distillation of the ether, and two vacuum distillations, 11 g of  $\alpha, \beta, \beta$ -trifluoro-p-methylstyrene (40%) was obtained with b. p.  $91.5^\circ$  (70 mm);  $n_D^{20}$  1.4810;  $d_4^{20}$  1.175; found MR 41.66; calculated MR 41.97. Found: C 62.97, 62.95; H 4.02, 4.00; F 32.95, 33.05%.  $\text{C}_9\text{H}_7\text{F}_3$ . Calculated: C 62.79; H 4.07; F 33.14%.

Preparation of  $\alpha, \beta, \beta$ -trifluoro-o-methylstyrene. Under the same conditions under argon 450 ml of an ether solution of o-tolylolithium (0.17 M; 17.4 g) was cooled to  $-78^\circ$  and an excess of tetrafluoroethylene (0.5 M; 50 g) was passed in during the course of 2 hr. Sixteen grams of  $\alpha, \beta, \beta$ -trifluoro-o-methylstyrene (55%) was obtained with b. p.  $79^\circ$  (75 mm);  $n_D^{20}$  1.4688;  $d_4^{20}$  1.140; found MR 42.70; calculated MR 41.97. Found: C 63.43, 63.36; H 3.66, 3.61; F 32.99; 33.02%.

Preparation of  $\alpha, \beta, \beta$ -trifluoro-m-methylstyrene. Under the same conditions under argon 280 ml of an ether solution of m-tolylolithium (0.2 M; 19.6 g) was cooled to  $-78^\circ$  and an excess of tetrafluoroethylene (0.35 M; 35 g) was passed in during the course of 2 hr. Sixteen grams of  $\alpha, \beta, \beta$ -trifluoro-m-methylstyrene (46.4%) was obtained with b. p.  $87.5^\circ$  (70 mm);  $n_D^{20}$  1.4795;  $d_4^{20}$  1.821; found MR 41.28; calculated MR 41.97. Found: C 63.20, 63.30; H 4.05, 4.01; F 32.95%.

Preparation of  $\alpha, \beta, \beta$ -trifluorostyrene. Under the same conditions under argon 200 ml of an ether solution of phenyllithium (0.15 M; 13.3 g) diluted with 150 ml of absolute ether was cooled to  $-78^\circ$ , and at this temperature an excess of tetrafluoroethylene (0.35 M; 35 g) was passed in during the course of 2 hr. Yield 7.4 g of  $\alpha, \beta, \beta$ -trifluorostyrene (30%) with b. p.  $62-63^\circ$  (75 mm);  $n_D^{20}$  1.4760;  $d_4^{20}$  1.220; found MR 36.53; calculated MR 37.20. Mole wt. 153.9-154.0 (calculated 158.0). Literature data [3]: b. p.  $68^\circ$  (75 mm); [8]: b. p.  $67-68^\circ$  (70 mm);  $n_D^{20}$  1.4731. Found: C 60.90, 61.00; H 3.02, 3.06; F 35.95, 36.00%.  $C_8H_5F_3$ . Calculated: C 60.76; H 3.16; F 36.07%.

#### SUMMARY

1.  $\alpha, \beta, \beta$ -Trifluoromethylstyrenes (ortho, meta, and para) have been prepared for the first time.
2. The IR spectra of four  $\alpha, \beta, \beta$ -trifluorostyrenes have been determined.

#### LITERATURE CITED

1. R. Meier and F. Böhler, Chem. Ber. 90, 2344 (1957).
2. P. Tarrant and D. A. Warner, J. Amer. Chem. Soc. 76, 1624 (1954); U.S. pat. 2804484 (1957).
3. S. Dixon, J. Organ. Chem. 21, 400 (1956).
4. D. I. Livingston, P. M. Kamath, and R. S. Corley, J. Polymer Sci. 20, 485 (1956); W. G. Barb, J. Polymer Sci. 37, 515 (1959).
5. K. S. Pitzer, L. Guttman, and E. F. Westrum, J. Amer. Chem. Soc. 68, 2209 (1946).
6. L. Bellamy, Infrared Spectra of Molecules [Russian translation] (IL, Moscow, 1957).
7. A. V. Zimin, S. V. Churmanteev, A. V. Gubanova, and A. D. Verina, Doklady Akad. Nauk SSSR 126, 784 (1959).
8. S. G. Cohen, H. T. Wolosinski, and P. J. Scheuer, J. Amer. Chem. Soc. 71, 3439 (1949).

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. Some or all of this periodical literature may well be available in English translation. A complete list of the cover-to-cover English translations appears at the back of this issue.

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# FLUORINATED STYRENES

## COMMUNICATION 6. $\alpha$ -DIFLUOROMETHYLSTYRENES AND $\alpha$ -TRIFLUOROMETHYLSTYRENES

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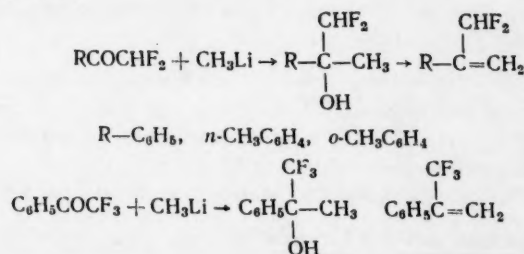
Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*,

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Original article submitted June 1, 1960

$\alpha$ -Trifluoromethylstyrene and  $\alpha$ -difluoromethylstyrene have been mentioned in a patent [1] as monomers which give stable polymers and copolymers suitable for the production of technical fiber. More recently a synthesis of  $\alpha$ -trifluoromethylstyrene through phenylmagnesium bromide has been published and the constants of this compound have been reported [2].

The problem of the synthesis of styrenes of this class for the investigation of their polymerization was presented to us [3]. Thus,  $\alpha$ -difluoromethylstyrene,  $\alpha$ -difluoromethyl-p-methylstyrene,  $\alpha$ -difluoromethyl-o-methylstyrene,  $\alpha$ -trifluoromethylstyrene, and  $\alpha$ -trifluoromethyl-p-fluorostyrene were synthesized. The synthesis of these compounds was carried out by the following route:



Furthermore, starting from phenylmagnesium bromide and p-fluorophenylmagnesium bromide with trifluoroacetone (through the carbinol stage)  $\alpha$ -trifluoromethylstyrene and  $\alpha$ -trifluoromethyl-p-fluorostyrene were prepared. The most convenient method was the use of methyl lithium and the readily available  $\omega$ -difluoroacetophenones or  $\omega$ -trifluoroacetophenones prepared from  $\text{RLi}$  and fluorinated acids [4] or diethylamides of the acids [5]. Condensations of methyl lithium with fluorinated acetophenones were carried out at a temperature of  $-20$  to  $-25^\circ$  in ether medium and the tertiary carbinols were obtained in 80-95% yield. Dehydration of the carbinols took place readily under the action of phosphorus pentoxide to yield 65-85% of the styrene. We further introduced a very simple method for the synthesis of p-chlorostyrene.

## EXPERIMENTAL

The organolithium compounds were prepared by the usual methods under nitrogen or argon. The fluorinated compounds were analyzed either by combustion of a weighed sample with sodium peroxide with subsequent titration with thorium nitrate to determine the fluorine content or by elementary analysis by the method of Zimin et al. [6].

**Preparation of o-methyl- $\omega,\omega$ -difluoroacetophenone.** In an apparatus for low temperature condensations under argon 250 ml of an ether solution of o-tolyl lithium (24.5 g; 0.25 M) was cooled to  $-75^\circ$ , and 33.7 g of freshly distilled diethylamide of difluoroacetic acid was added at this temperature during the course of 40 minutes, with vigorous stirring, then the mixture was stirred for 1 hr more. It was then decomposed by pouring into ice water acidified with hydrochloric acid. Yield 28 g (65.7%) of o-methyl- $\omega,\omega$ -difluoroacetophenone with b. p.  $61-63^\circ$  (4 mm);  $n_D^{20}$  1.4995. Found: F 23.01, 22.80%.  $\text{C}_9\text{H}_8\text{F}_2\text{O}$ . Calculated: F 22.35%.

Preparation of p-methyl- $\omega,\omega$ -difluoroacetophenone. In an apparatus for low temperature condensations under argon 250 ml of an ether solution of p-tolyl lithium (24.5 g; 0.25 M) was cooled to  $-75^{\circ}$ , and 33.7 g of freshly distilled diethylamide of difluoroacetic acid was added at this temperature during the course of 40 minutes, with good stirring, then the mixture was stirred for 1 hr more. The mixture was then decomposed by pouring it into ice water acidified with hydrochloric acid. After the usual treatment and distillation of the ether, crystals were obtained; they were filtered by suction, and washed with hexane and pentane. After recrystallization from absolute methyl alcohol, 22 g (51.7%) of p-methyl- $\omega,\omega$ -difluoroacetophenone was obtained with m. p.  $48-51^{\circ}$ . Found: F 23.10, 22.95%. Calculated: F 22.94%.

Preparation of difluoromethylmethyl-o-tolylcarbinol. In an apparatus for low temperature condensations under argon 120 ml of an ether solution of methyllithium (1.97 g; 0.09 M) was cooled to  $-25^{\circ}$ . At this temperature 15.7 g (0.09 M) of difluoromethyl-o-tolyl ketone in 50 ml of absolute ether was added at such a rate that the temperature did not rise above  $-20^{\circ}$ . At the end of the addition the reaction mixture was stirred for 30 minutes and treated in the usual manner. Yield 12 g of difluoromethylmethyl-o-tolylcarbinol; b. p.  $88.5-89^{\circ}$  (3 mm);  $n_D^{20}$  1.5039.

Preparation of  $\alpha$ -difluoromethyl-o-methylstyrene. In a flask with a reflux condenser were placed under nitrogen 10 g of difluoromethylmethyl-o-tolylcarbinol (0.053 M), 3.96 g of phosphorus pentoxide (0.026 M), 0.3 g of copper powder, and 100 ml of dry benzene. The reaction mixture was heated for 4.5 hr at the boiling point of benzene. Yield 3.5 g of  $\alpha$ -difluoromethyl-o-methylstyrene (42%); b. p.  $98^{\circ}$  (50 mm);  $n_D^{20.5}$  1.4910. Found: C 71.47, 71.48; H 5.99, 6.00; F 22.50, 22.49%. Calculated: C 71.42; H 5.95; F 22.63%.

Preparation of difluoromethylmethyl-p-tolylcarbinol. In a special apparatus for work at low temperatures under argon was placed 130 ml of an ether solution of methyllithium (2.2 g; 0.1 M) and the mixture was cooled to  $-20^{\circ}$ . At this temperature and with good stirring 17.0 g (0.1 M) of difluoromethyl o-tolyl ketone in 50 ml of absolute ether was added. The temperature during the time of reaction was maintained at  $-20$  to  $-22^{\circ}$ . Stirring was continued for 2 hr more. After the usual treatment, 10 g of difluoromethyl-p-tolylcarbinol (53.6%) was obtained; b. p.  $92^{\circ}$  (3 mm);  $n_D^{20}$  1.5009.

Preparation of  $\alpha$ -difluoromethyl-p-methylstyrene. In a flask with a reflux condenser were placed, under nitrogen, 8.5 g of difluoromethylmethyl-p-tolylcarbinol (0.045 M), 3.19 g of phosphorus pentoxide (0.0225 M), 0.3 g of copper powder, and 100 ml of dry benzene. The reaction mixture was heated for 4.5 hr at the boiling point of benzene. Yield 4.1 g of  $\alpha$ -difluoromethyl-p-methylstyrene (54%); b. p.  $103^{\circ}$  (50 mm);  $n_D^{20}$  1.4898. Found: C 72.18, 71.98; H 5.60, 5.56; F 22.0, 22.02%.  $C_{10}H_{10}F_2$ . Calculated: C 71.43; H 5.93; F 22.62%.

Preparation of  $\alpha$ -trifluoromethyl- $\alpha$ -methylbenzyl alcohol. From methyllithium and trifluoroacetophenone. The reaction was carried out in an apparatus for condensations at low temperatures under nitrogen. In the apparatus was placed 255 ml of an ether solution of methyllithium containing 4.4 g of methyllithium (0.2 M), which then was cooled to  $-30^{\circ}$ . At this temperature, with vigorous stirring, the addition of 34.8 g (0.2 M) of trifluoroacetophenone [7] in 50 ml of absolute ether was started at such a rate that the temperature did not rise above  $-20^{\circ}$ ; the addition required 2 hr. Then stirring was continued for another 2 hr at  $-20^{\circ}$ , and the mixture was decomposed by pouring it into ice with dilute hydrochloric acid. After the usual treatment 32.5 g of  $\alpha$ -trifluoromethyl- $\alpha$ -methylbenzyl alcohol was obtained; b. p.  $91-91.5^{\circ}$  (21 mm);  $71-72^{\circ}$  (10 mm); yield 79%;  $n_D^{20}$  1.4658. According to literature data [2]: b. p.  $62-66^{\circ}$  (4.5 mm);  $n_D^{20}$  1.4656.

From phenylmagnesium bromide and trifluoroacetone. An ether solution of phenylmagnesium bromide was prepared from 7.3 g of magnesium and 47.1 g of bromobenzene in 200 ml of absolute ether. This solution was cooled under nitrogen to  $-10^{\circ}$ , and with vigorous stirring over a period of 1 hr 40 g of trifluoroacetone in 50 ml of absolute ether previously cooled to  $-30^{\circ}$  was added. The dropping funnel for the addition of this solution was cooled to  $-10^{\circ}$ . At the end of the addition stirring was continued for 2 hr, with gradual raising of the temperature to that of the room, and the mixture was then left to stand until the next day. The reaction mixture was decomposed by pouring into ice with the addition of dilute hydrochloric acid. Yield 46 g of  $\alpha$ -trifluoromethyl- $\alpha$ -methylbenzyl alcohol (70%).

Preparation of  $\alpha$ -trifluoromethylstyrene. The dehydration of 40 g of  $\alpha$ -trifluoromethyl- $\alpha$ -methylbenzyl alcohol was carried out by heating with 36 g of phosphorus pentoxide on an oil bath in a current of nitrogen and distilling the products of the reaction off at a bath temperature of  $160-165^{\circ}$  (at the end of the distillation up to  $185^{\circ}$ ). The material obtained was diluted with ether and washed with 5% sodium hydroxide solution and with a saturated solution of calcium chloride, and dried after the usual treatment. Yield 30 g of  $\alpha$ -trifluoromethylstyrene (82%); b. p.  $80.5^{\circ}$  (77 mm);  $n_D^{20}$  1.4620;  $d_4^{20}$  1.172; found MR 41.29; calculated MR 41.97. According to literature data [2]:  $n_D^{21}$  1.4603;  $d_4^{21}$  1.167.

**Preparation of  $\alpha$ -difluoromethyl- $\alpha$ -methylbenzyl alcohol.** The reaction was carried out in an apparatus for condensations at low temperatures under nitrogen. In the apparatus was placed an ether solution of methyl lithium containing 4 g of methyl lithium (prepared from methyl chloride). The mixture was cooled to  $-30^\circ$  and at this temperature 22.7 g of  $\omega,\omega$ -difluoroacetophenone [8] (0.15 M) in 50 ml of ether was added dropwise, with stirring. The temperature of the reaction mixture was not allowed to rise above  $-25^\circ$  and the addition took 2.5 hr. Then the mixture was stirred for 1.5 hr more at a temperature of about  $-20^\circ$  and decomposed by pouring it into water and ice acidified with dilute hydrochloric acid. Yield 23.2 g of  $\alpha$ -difluoromethyl- $\alpha$ -methylphenylcarbinol (92.5%); b. p.  $81^\circ$  (7 mm);  $n_D^{20}$  1.4929. Found: F 21.84, 21.65%.  $C_9H_{10}OF_2$ . Calculated: F 22.09%.

**Preparation of  $\alpha$ -difluoromethylstyrene.** A solution of 10.5 g of  $\alpha$ -difluoromethyl- $\alpha$ -methylbenzyl alcohol (0.06 M) in 100 ml of benzene was prepared and 4.2 g of phosphorus pentoxide (0.03 M) in 20 ml of benzene was added. The mixture was refluxed with moderate boiling under nitrogen for 5 hr on a glycerol bath. Then the solution was poured off, dried with sodium sulfate with a little added copper powder, the benzene was distilled off, and the residue was distilled. Yield 6.2 g (60.5%) of  $\alpha$ -difluoromethylstyrene; b. p.  $90.0-90.5^\circ$  (40 mm);  $n_D^{20}$  1.4980. Found: F 24.35, 24.45%.  $C_9H_8F_2$ . Calculated: F 22.09%.

**Preparation of  $\alpha$ -trifluoromethyl- $\alpha$ -methyl-p-fluorobenzyl alcohol.** p-Fluorophenylmagnesium bromide was prepared in the usual way from 26.3 g (0.15 M) of p-fluorobromobenzene in 200 ml of absolute ether and 3.7 g (0.15 M) of magnesium. It was cooled to  $-10^\circ$  and over the course of 45 minutes 18.4 g (10% excess) of trifluoroacetone in 40 ml of absolute ether (cooled to  $-50^\circ$ ) was added dropwise with vigorous stirring, the stirring was continued for 3 hr more at a temperature of about  $0^\circ$ , and the mixture was left at room temperature overnight. After the usual treatment and distillation in vacuum, 20.5 g (65%) of  $\alpha$ -trifluoromethyl- $\alpha$ -methyl-p-fluorobenzyl alcohol was obtained; b. p.  $83-84^\circ$  (17 mm). Found: F 36.82, 36.64%.  $C_9H_8OF_4$ . Calculated: F 36.97%.

**Preparation of  $\alpha$ -trifluoromethyl-p-fluorostyrene.** Dehydration of  $\alpha$ -trifluoromethyl- $\alpha$ -methyl-p-fluorobenzyl alcohol (16.5 g) was carried out by treating with 15 g of phosphorus pentoxide and gradually heating the mixture on an oil bath under nitrogen. Distillation began at a bath temperature of  $170-180^\circ$  and continued at this temperature for 1 hr. The mixture was further heated for 30 minutes at  $190-200^\circ$ . A total of 14 g of crude product was obtained. After distillation, 11.5 g (76%) of  $\alpha$ -trifluoromethyl-p-fluorostyrene with b. p.  $53^\circ$  (20 mm) and 1.5 g of the starting carbinol were isolated. Found: F 39.76, 39.80%.  $C_9H_6F_4$ . Calculated: F 40.0%.

**Preparation of p-chlorophenylmethylcarbinol.** In an apparatus filled with argon was placed 270 ml of 0.64 N ether solution of n-butyllithium and at a temperature of  $20^\circ$ , 30.7 g of p-chlorobromobenzene in 50 ml of absolute ether was added, with vigorous stirring, over a period of 20 minutes, then stirring was continued for 10 minutes more, and an excess (10 g) of acetaldehyde in 10 ml of absolute ether was added at a temperature not higher than  $25^\circ$ . The mixture was decomposed by pouring into ice with hydrochloric acid; after the usual treatment p-chlorophenylcarbinol [9] (80-85%) was obtained; b. p.  $118-121^\circ$  (12 mm).

**Preparation of p-chlorostyrene.** Dehydration of 31.5 g of p-chlorophenylmethylcarbinol with 3 g of potassium acid sulfate was carried out under the usual conditions [8]. After treatment about 20 g of p-chlorostyrene was obtained with b. p.  $75-76^\circ$  (19 mm);  $n_D^{20}$  1.5665;  $n_D^{20}$  1.5646; yield 60-65%. According to the data in the literature [10]: b. p.  $39^\circ$  (2 mm);  $n_D^{20}$  1.5648.

## SUMMARY

1. Methods have been developed for the synthesis of  $\alpha$ -difluoromethylstyrenes and  $\alpha$ -trifluoromethylstyrenes.
2.  $\alpha$ -Difluoromethylstyrene,  $\alpha$ -difluoromethyl-o-methylstyrene,  $\alpha$ -difluoromethyl-p-methylstyrene, and  $\alpha$ -trifluoromethyl-p-fluorostyrene have been described for the first time.

## LITERATURE CITED

1. Chem. Abstr. 43, 8209 (1949); U. S. Patents 2,475,299 and 2,475,423.
2. P. Tarrant and R. E. Taylor, J. Organ. Chem. 24, 238 (1958).
3. A. R. Gantmakher, Yu. L. Spirin, and S. S. Medvedev, Vysokomolekulyarnye soedineniya 1, 1526 (1959).
4. K. T. Dishard and R. Levine, J. Amer. Chem. Soc. 78, 2268 (1956); 77, 3656 (1955); J. D. Park, R. E. Noble, and J. R. Lacher, J. Organ. Chem. 23, 1396 (1956); M. M. Nad', T. V. Talalaeva, G. V. Kazennikova, and K. A. Kocheshkov, Izv. AN SSSR, Otd. Khim. Nauk 1959, 272; D. A. Rausch, A. M. Lovelace, and L. E. Coleman, J. Amer. Chem. Soc. 79, 4893 (1957); J. Organ. Chem. 21, 1328 (1956).

5. N. A. Zaitseva, E. M. Panov, and K. A. Kocheshkov, *Izv. AN SSSR, Otd. Khim. Nauk* 1961, 000.
6. A. V. Zimin, S. V. Churmanteev, A. V. Gubanova, and A. D. Verina, *Doklady Akad. Nauk SSSR* 126, 784 (1959).
7. T. McGroth and R. Levine, *J. Amer. Chem. Soc.* 77, 3656 (1955).
8. M. M. Nad', T. V. Talalaeva, G. V. Kazennikova, and K. A. Kocheshkov, *Izv. AN SSSR, Otd. Khim. Nauk* 1959, 272.
9. D. Woodcock, *J. Chem. Soc.* 1949, 253.
10. G. S. Marvel and G. L. Schertz, *J. Amer. Chem. Soc.* 65, 2054 (1943).

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# CONDENSATION OF *p*-TRIMETHYLSILYLBENZALDEHYDE WITH ALDEHYDES AND KETONES

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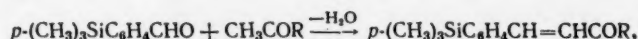
Translated from *Izvestiya Akademii Nauk SSSR, Oteelenie Khimicheskikh Nauk*,

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Original article submitted July 4, 1960

In a previous communication [1] some properties of *p*-trimethylsilylbenzaldehyde have been discussed. It has been shown that *p*-trimethylsilylbenzaldehyde gives the qualitative reactions characteristic of a carbonyl group and enters freely into addition reactions with various organic reagents (sodium bisulfite, semicarbazide, 2,4-dinitrophenylhydrazine, hydroxylamine, ammonia, and aromatic amines).

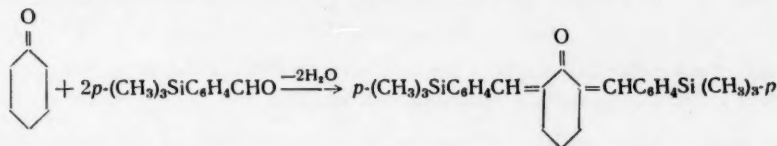
The present work was devoted to a study of the condensation of *p*-trimethylsilylbenzaldehyde with aldehydes and ketones in the presence of aqueous solutions of alkalis as catalysts. Condensation was carried out with acetone, pinacoln, acetophenone, cyclohexanone, acetaldehyde, and formaldehyde. In the study of the condensation reaction of *p*-trimethylsilylbenzaldehyde with ketones it was found that when there is one active methylene group in the ketone the reaction proceeds in a well defined manner according to the scheme



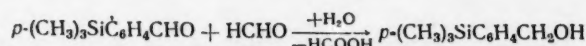
where R = C<sub>6</sub>H<sub>5</sub>; C(CH<sub>3</sub>)<sub>3</sub>.

With two active methylene groups in the molecule of the ketone (for example, acetone, cyclohexanone) further condensation is possible at the expense of the second methylene group. Thus, when *p*-trimethylsilylbenzaldehyde was condensed with acetone in a 1:1 molar ratio, *p*-trimethylsilylbenzalacetone was obtained, but with a 2:1 ratio *p*-trimethylsilylbenzalacetone was absent and a tetramer was formed, apparently di-(*p*-trimethylsilylbenzal)acetone.

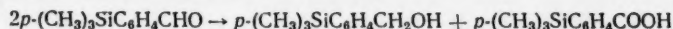
In the reaction with cyclohexanone, as a result of its specific properties, with the same ratios and reaction conditions we were able to obtain only 1,3-di-(*p*-trimethylsilylbenzal)cyclohexanone



*p*-Trimethylsilylbenzaldehyde reacted with acetaldehyde according to the usual scheme of aldol condensation, but with formaldehyde the reaction proceeded with the formation of an alcohol according to the scheme



In spite of the easy oxidation of *p*-trimethylsilylbenzaldehyde, we were able to carry out a Cannizzaro reaction in the presence of an aqueous solution of potassium hydroxide; in this process one molecule of the aldehyde was reduced to alcohol, the other was oxidized to acid.



## EXPERIMENTAL

Ketones and aldehydes used for condensation were purified by the usual methods of organic chemistry and their physical constants agreed well with the literature data. The methods of determining the physical constants have been

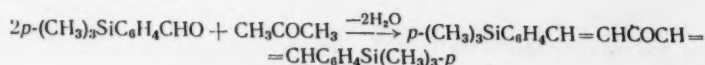
described previously [2, 3]. The molecular refractions were calculated as described by Vogell [4]. Silicon was determined in a number of the condensation products by the method of wet combustion with a mixture of fuming nitric acid and oleum. The elementary composition of the compounds was determined by combustion of a microsample of the compound in an empty tube.\* Nitrogen was determined in the semicarbazones by microcombustion by the Dumas method.

p-Trimethylsilylbenzaldehyde prepared by a previously described method [1] had the b. p. 87.4-87.8° (5 mm); 118-119° (15 mm);  $n_D^{20}$  1.5245; Semicarbazone: b.p. 200-201°. Found Si 12.11, 12.18; N 17.91, 17.78%.  $C_{11}H_{17}SiN_3$ . Calculated: Si 11.94; N 17.85%. All experiments were carried out in an atmosphere of nitrogen.

#### Reaction of p-Trimethylsilylbenzaldehyde with Acetone

p-Trimethylsilylbenzalacetone. A mixture of 6.4 g (0.11 M) of acetone and 7.2 g (0.04 M) of p-trimethylsilylbenzaldehyde with 1 ml of 10% sodium hydroxide solution was stirred vigorously at room temperature for 5 hr. Then dilute hydrochloric acid was added to the reaction mixture to an acid reaction and the product was extracted from the aqueous mixture with benzene. After the benzene had been distilled off and the residue distilled in vacuum, 6.1 g (74% of theoretical) of p-trimethylsilylbenzalacetone was obtained as a slightly yellowish liquid with b. p. 127.5-128.5° (1 mm); 139.4-139.7° (5 mm);  $n_D^{20}$  1.5670;  $d_4^{20}$  1.0215; found MR 69.84; calculated MR 69.16. On standing, the liquid set to a solid mass with m. p. 31-32°. Found: Si 12.48, 12.61; C 71.30, 71.47; H 8.29, 8.13%; mole wt 219.2; 217.1.  $C_{13}H_{18}SiO$ . Calculated: Si 12.86; C 71.50; H 8.31%; mole wt. 218.4. The semicarbazone of p-trimethylsilylbenzalacetone formed lustrous yellowish plates with m. p. 197-198°. Found: Si 9.86, 9.93; N 15.02, 15.19%.  $C_{14}H_{21}SiN_3O$ . Calculated: Si 10.20; N 15.26%.

Di-(p-trimethylsilylbenzal)acetone. The synthesis was carried out according to the reaction



by the following method: to a solution of 5 g of sodium hydroxide in 50 ml of water and 40 ml of ethyl alcohol was added with vigorous stirring a mixture of 9 g (0.05 M) of p-trimethylsilylbenzaldehyde with 1.5 g (0.025 M) of acetone. The reaction mixture was stirred at room temperature for 5 hr. During this process a brownish oily product was formed. Similar results were obtained upon more prolonged stirring and under conditions of cooling and heating the reaction mixture. The oily product was extracted from the reaction mixture with benzene. After the benzene had been distilled off in vacuum, a brown viscous tar was obtained which was converted to a solid yellow mass by washing three times with hot alcohol. Recrystallized from hot alcohol the product had the m. p. 190-193°; its elementary composition approximated the formula  $C_{23}H_{30}Si_2O$ , i.e., di-(p-trimethylsilylbenzal)acetone. Found: C 71.92, 72.27; H 7.98, 7.29; Si 13.45, 14.16%.  $C_{23}H_{30}Si_2O$ . Calculated: C 72.54; H 7.97; Si 14.84%.

Determination of the molecular weight in benzene gave a value equivalent to four times the above formula. Mol. wt. found 1541; 1528.  $C_{22}H_{30}Si_2O_4$ . Calculated mol. wt. 1504.

It may be assumed that the conditions of reaction and recrystallization of the product obtained from alcohol in the sunlight lead to further condensation of the primary reaction products, as takes place in the case of dibenzalacetone [5].

#### p-Trimethylsilylbenzalpinacolin

A mixture of 8 g (0.045 M) of p-trimethylsilylbenzaldehyde, 4 g (0.04 M) of pinacolin, and 15 ml of ethyl alcohol with 4 ml of 10% sodium hydroxide solution was shaken vigorously for 48 hr. After 20 days standing the mixture was diluted with an equal volume of water; the p-trimethylsilylbenzalpinacolin was extracted with ether; the ether extract was washed with water and dried with calcium chloride, the ether was distilled off, and the residue was distilled in vacuum. On repeated distillation in vacuum, 7.2 g (61% of theoretical) of pure product was obtained with b. p. 153-153.6° (4 mm);  $n_D^{20}$  1.5448; the product very quickly solidified to a slightly yellowish mass with m. p. 34-35°, readily soluble in alcohol, ether, and benzene. Found: Si 10.36, 10.37; C 73.76, 73.66; H 9.42, 9.34%; mole wt. 260; 261.  $C_{16}H_{24}SiO$ . Calculated: Si 10.78; C 73.78; H 9.29%; mole wt. 260.

#### P-Trimethylsilylbenzalacetophenone

To an alkali solution, prepared by dissolving 2.18 g (0.055 M) of sodium hydroxide in a mixture of 19.5 ml of water and 12.5 ml of 95% ethyl alcohol, was added, with vigorous stirring and cooling to 13-15°, 5.2 g (0.043 M) of

acetophenone with b. p. 76-77° (10 mm) and 7.7 g (0.043 M) of p-trimethylsilylbenzaldehyde. After 3 hr stirring the reaction mixture was kept at +2 to 0° for 15 hr. In this time a paste formed which consisted of a fine yellowish suspension and an almost colorless liquid. The mixture was filtered with suction and the precipitate was washed with water, then with cold alcohol, dried in a desiccator over calcium chloride, and recrystallized twice from alcohol. The weight of the recrystallized product was 5.3 g; m. p. 69-69.7°. The filtrate consisted of two layers, aqueous and oily. The oily product was separated, dried with sodium sulfate, and after distillation in vacuum another 3 g of the main product was isolated from it with b. p. 210-212° (4 mm); m. p. 69-69.5°. In all, 8.3 g (67% of theoretical) of p-trimethylsilylbenzalacetophenone was obtained as light yellow lustrous plates, readily soluble in ether and benzene, more difficultly so in alcohol. Found: Si 9.84, 9.91; C 77.11, 77.13; H 6.98, 6.86%; mole wt. 278.1; 279.3.  $C_{18}H_{20}SiO$ . Calculated: Si 10.02; C 77.09; H 7.19%; mole wt 280.4.

### 1,3-Di-(p-trimethylsilylbenzal)cyclohexanone

When a mixture of 8 g (0.045 M) of p-trimethylsilylbenzaldehyde and 2 g (0.02 M) of cyclohexanone was shaken for 30 hr with 8 ml of 10% sodium hydroxide solution in 50 ml of ethyl alcohol, a copious yellow precipitate was formed. After filtration, washing with water and alcohol, drying, and recrystallization from alcohol, 6.4 g of 1,3-di-(p-trimethylsilylbenzal)cyclohexanone was obtained; m. p. 145°; yield 76.5% of theoretical. Found: Si 13.40, 13.18; C 74.33, 73.98; H 7.92, 8.01%; mole wt. 416.0; 419.3.  $C_{26}H_{34}SiO$ . Calculated: Si 13.42; C 74.58; H 8.19%; mole wt. 418.7.

### Reaction of p-Trimethylsilylbenzaldehyde with Formaldehyde

To a mixture of 7.2 g (0.04 M) of p-trimethylsilylbenzaldehyde, 10 ml of formalin (0.12 M of formaldehyde) and 10 ml of methyl alcohol heated to 60-65° was added 6.8 g (0.12 M) of potassium hydroxide in 5 ml of water. Then the reaction mixture was heated on a water bath for 2 hr, cooled, and diluted with 30 ml of water. An oily layer separated; the aqueous layer was extracted with benzene. The oil and the benzene extracts were combined, washed with sodium bisulfite and with water, and dried with sodium sulfate. The benzene was distilled off and the residue was distilled in vacuum. Yield 4.7 g (65.2% of theoretical) of p-trimethylsilylphenylcarbinol with b. p. 131.5-132° (11 mm);  $n_D^{20}$  1.5143;  $d_4^{20}$  0.9602; found MR 56.57; calculated MR 56.25. Literature data [6]: b. p. 139° (16 mm);  $n_D^{20}$  1.5140;  $d_4^{20}$  0.9605. Found: Si 15.43, 15.28%.  $C_{10}H_{16}SiO$ . Calculated: Si 15.58%.

### p-Trimethylsilylcinnamaldehyde

To a mixture of 20 ml of ethyl alcohol, 9 g (0.05 M) of p-trimethylsilylbenzaldehyde, and 5 g (0.1 M) of acetaldehyde was added slowly, with cooling, 120 ml of a 1% solution of sodium hydroxide, and the reaction mixture was vigorously stirred for 5 hr. Then 10 g of sodium chloride was added to the mixture and the product was extracted with ether. The ether extract was dried with sodium sulfate, the ether was distilled off, and the residue was distilled in vacuum in an atmosphere of nitrogen. Yield 8.6 g (83.4% of theoretical) of p-trimethylsilylcinnamaldehyde, a clear, colorless oil with a weak cinnamon odor; b. p. 97-98° (3 mm); 108-109° (11 mm);  $n_D^{20}$  1.5210;  $d_4^{20}$  0.9837; found MR 63.52; calculated MR 63.23. Found: Si 13.51, 13.74; C 70.42, 70.87; H 7.81, 8.01%; mole wt. 205.4; 203.1.  $C_{12}H_{18}SiO$ . Calculated: Si 13.61; C 70.53; H 7.89%; mole wt. 204.4. The semicarbazone, purified by recrystallization from alcohol, melted at 198-200°. Found: Si 10.81, 10.79; N 16.24, 16.01%.  $C_{13}H_{19}SiN_3O$ . Calculated: Si 10.74; N 16.08%.

### Cannizzaro Reaction

In a 50-ml flask were placed 9 g (0.05 M) of p-trimethylsilylbenzaldehyde and a solution of 5 g of potassium hydroxide in 5 ml of water. The mixture was shaken for 2 hr, until a stable emulsion formed which was kept for 20 hr at room temperature. To the crystalline mass that separated (potassium p-trimethylsilylbenzoate) was added 60 ml of water until the mass entirely dissolved; the p-trimethylsilylphenylcarbinol was extracted with ether; the ether extract was dried with sodium sulfate, the ether was distilled off, and from the residue 3.5 g (77.8% of theoretical) of p-trimethylsilylphenylcarbinol was obtained by distillation with b. p. 138-139° (16 mm);  $n_D^{20}$  1.5142. Found: Si 15.31, 15.65%.  $C_{10}H_{16}SiO$ . Calculated: Si 15.58%. The aqueous alkali solution was acidified with hydrochloric acid, whereupon p-trimethylsilylbenzoic acid precipitated, which after recrystallization from a large amount of hot water and then from ligroin melted at 117-118°. Literature data [6]: b. p. 117-118°. Found: Si 13.41, 14.48%.  $C_{10}H_{14}SiO_2$ . Calculated: Si 14.46%.

Analyses were made by Yu. N. Platonov, to whom the authors express their appreciation.

### SUMMARY

1. The condensation of p-trimethylsilylbenzaldehyde with aldehydes and ketones has been studied.
2. A number of tetra-substituted silanes have been prepared, the organic radicals of which contain different functional groups (carbonyl, carboxyl, hydroxyl) and their physicochemical constants have been determined. Seven of the compounds prepared were synthesized for the first time.
3. The Si-C<sub>ar</sub> bond in these compounds is stable to the action of 10-20% solutions of alkalis and acids.

### LITERATURE CITED

1. B. N. Dolgov, N. E. Glushkova, and N. P. Kharitonov, *Izv. AN SSSR, Otd. Khim. Nauk* **1960**, 351.
2. M. G. Yeronkov, B. N. Delgov, and N. F. Zapalova, *Uch. zap. LGU, seriya Khim.* **12**, 161 (1953).
3. B. N. Dolgov, N. P. Kharitonov, and M. G. Voronkov, *Zh. obshch. khimii* **24**, 1178 (1954).
4. A. J. Vogell, *J. Chem. Soc.* **1948**, 1838; A. J. Vogell, et al., *J. Chem. Soc.* **1952**, 514.
5. G. Glamician and P. Silber, *Ber.* **42**, 1386 (1909).
6. R. G. Severson, R. J. Rosscup, et al., *J. Amer. Chem. Soc.* **79**, 6540 (1957).

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. Some or all of this periodical literature may well be available in English translation. A complete list of the cover-to-cover English translations appears at the back of this issue.

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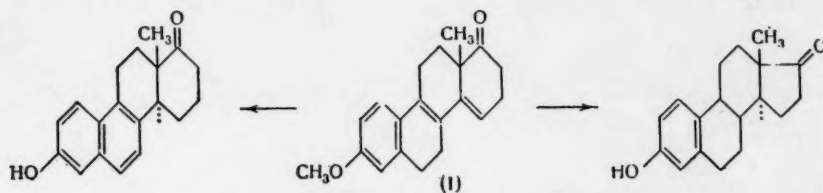
# SYNTHESIS OF 19-NORSTEROIDS BASED ON

## 3-METHOXY-D-HOMOEOSTRA-1,3,5(10),8,14-PENTAEN-17a-ONE

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I. V. Torgov

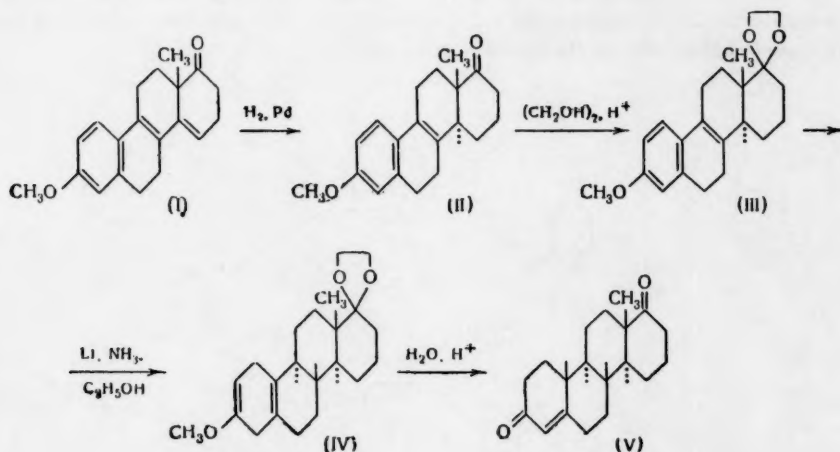
Institute of Chemistry of Natural Compounds, Academy of Sciences of the USSR  
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In previous communications the conversion of the readily available 3-methoxy-D-homoestra-1,3,5(10),8,14-pentaen-17a-one (I) to D-homoequilenin [1] and estrone [2] has been described.

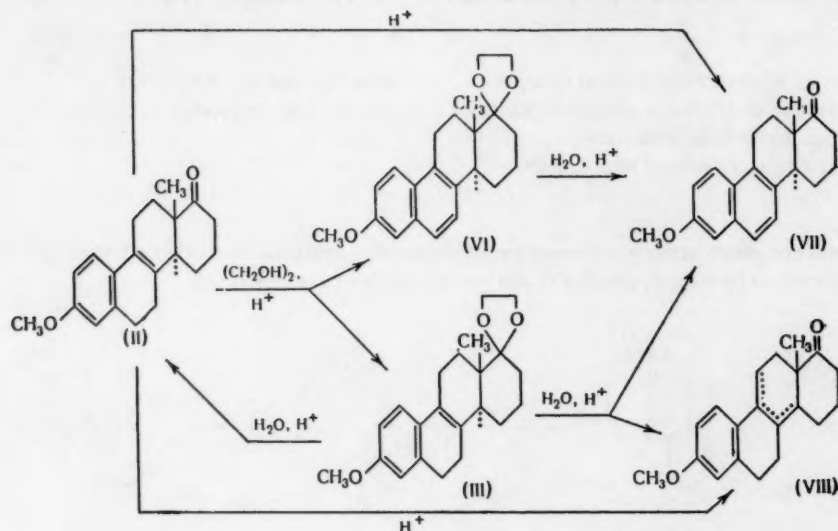


Naturally the idea arose of converting the ketone (I) not only to steroids with the aromatic ring A, which have an estrogenic effect, but also to 19-nor-3-ketosteroids and their derivatives, which might have androgenic, gestagenic, or anabolic activity. Pertinent examples are numerous in the literature. Thus, 19-nortestosterone has 30% of the activity of testosterone [3], 19-nor-17-ethynyltestosterone (Norlutin) is several times as active as progesterone [4], and 17-ethyl-19-nortestosterone has a strong anabolic effect [5].

We therefore undertook a study of the conversions of ketone (I), including the reduction of ring A by metals in liquid ammonia. When ketone (I) was hydrogenated, the previously described 3-methoxy-D-homoestra-1,3,5(10),8-tetraen-17a-one (II) was obtained; its ethylene ketal (III) on reduction with lithium and alcohol in liquid ammonia went to the ethylene ketal of 3-methoxy-D-homoestra-2,5(10)-dien-17a-one (IV), which on hydrolysis gave 19-nor-D-homoandrosta-4-dien-3,17a-dione (V).

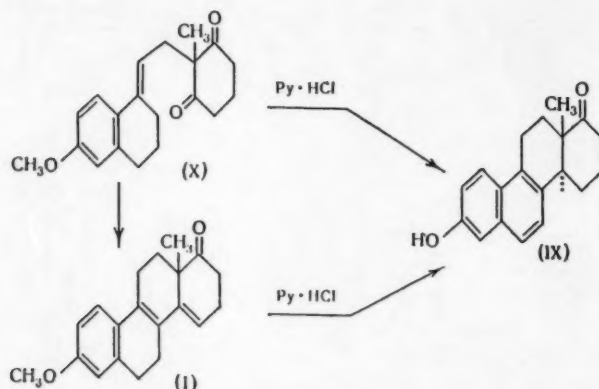


Since it has previously been shown that the ketal (IV) on dehydrogenation yields a derivative of estrone with the natural configuration [2], then consequently the ketal (IV) and the diketone (V) have an analogous configuration. It is interesting to note that when ketone (II) was converted to the ketal a side hydrogenation reaction took place and in addition to ketal (III) the ketal of the methyl ether of trans-D-homoequilenin (VI) was isolated. Hydrolysis of ketal (III) also was accompanied by dehydrogenation and isomerization, and as a result a complex mixture of materials was obtained, from which we succeeded in isolating the methyl ether of trans-D-homoequilenin (VII).

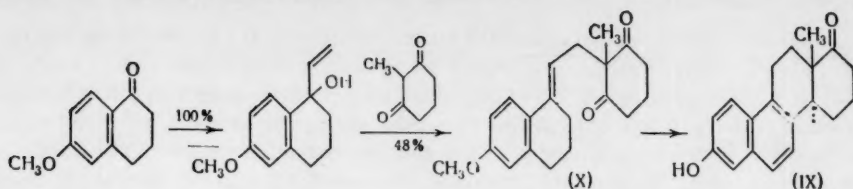


The ease of dehydrogenation of ketal (III) (apparently as a result of irreversible catalysis) is not anything exceptional and has been recorded in the literature. Thus, equilin, or  $\Delta^4$ -estrone, under the conditions of catalytic hydrogenation is converted to equilenin [6].

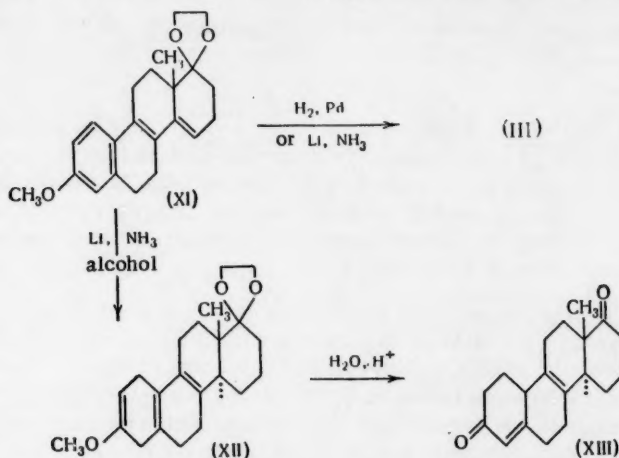
The starting ketone (II) upon heating in acid medium also undergoes isomerization and dehydrogenation. No doubt the isomerization takes place as a result of migration of a double bond, but the corresponding product (VIII) could not be separated into the individual compounds and as in the case of ketal (III) it was possible to isolate only the methyl ether of D-homoequilenin (VII). The ease of formation of the equilenin system was demonstrated also in the demethylation of ketone (I). In the first communication [1] the structure of D-homoestra-1,3,5,8,14-pentaen-3-ol-17a-one was ascribed to the demethylation product, but its UV spectrum agreed with the spectrum of trans-D-homoequilenin (IX) and their acetates did not show a depression in melting point. The demethylation of 3-methoxy-8,14-seco-D-homoestra-1,3,5(10),9-tetraen-14,17a-dione (X), by the cyclization of which ketone (I) is obtained, also leads to trans-D-homoequilenin (IX), even in good yield.



Thus, starting with 6-methoxytetralone, the synthesis of D-homoequilenin (IX) has been accomplished in a total of three stages with an over-all yield of 29%.



When ketone (I) reacted with ethylene glycol in the usual way, the corresponding ethylene ketal (XI) was obtained. Hydrogenation of the latter led to the ethylene ketal (III); the same results were obtained also by reduction by Birch's method with a fivefold excess of lithium. With a large excess of lithium in the presence of alcohol, reduction of the aromatic ring also occurred, but the double bond between the rings remained unaffected even if the reaction was carried out with a 35 fold excess of lithium (calculated on the double bonds).



The ethylene ketal of 3-methoxy-D-homoestra-2,5(10),8-trien-17a-one (XII) formed went over on hydrolysis to the unsaturated ketone (XIII) with one conjugated double bond, as follows from the UV spectrum, which has  $\lambda_{\max}$  235 m $\mu$ ;  $\log \epsilon$  4.30, close to the values for the diketone (V), while the conjugated dienones have maxima in the region 280-290 m $\mu$  [7]. The position of the second double bond is to some extent conjectural, although it is difficult to visualize its migration to any other unconjugated position.

#### EXPERIMENTAL

**Preparation of 6-methoxytetralin.** A mixture of 150 g of recrystallized nerolin with m. p. 71-72°, 200 ml of methanol, 6 ml of acetic acid, and 10 g of Raney nickel was hydrogenated in a one-liter, rotating autoclave at 130° and an initial hydrogen pressure of 150 atm. The hydrogen was mainly adsorbed in 2-2.5 hr. The catalyst was filtered off, the methanol was distilled off in vacuum, and by a double distillation 111 g (72%) of 6-methoxytetralin was obtained with b. p. 117-118° (8 mm);  $n_D^{20}$  1.5420. If the hydrogen pressure is low ( $\sim$  100 atm), the yield of the desired fraction sometimes falls to 50%.

**Preparation of 6-methoxytetralone.** To a solution of 150 g of 6-methoxytetralin in 750 ml of acetone was added at -5° over the course of an hour a solution of 140 g of chromic anhydride and 225 g of sulfuric acid in 565 ml of water; the mixture was stirred for 6 hr and left overnight. The next day the acetone layer was separated off and the aqueous layer was carefully extracted (10-15 times) with ether. The combined ether-acetone solution was neutralized with dry sodium carbonate, dried with magnesium sulfate, filtered, and a large part of the solvent was distilled off. The crystals that precipitated were filtered with suction and washed with cold methanol. The yield was 82 g of 6-methoxytetralone with m. p. 77-78°, sufficiently pure for the next reaction. By evaporation and

crystallization of the mother liquors it was possible to bring the yield to 92 g (56%). In another experiment 220 g of 6-methoxytetralone was obtained from 460 g of 6-methoxytetralin, but 135 g of the starting ether was recovered, so that the yield amounted to 61% taking into account the unreacted methoxytetralin.

Preparation of 1-vinyl-6-methoxytetralol-1 and condensation of it with methylidihydroresorcinol. The preparation of 1-vinyl-6-methoxytetralol-1 was carried out by the method described in [8]. A mixture of 6.5 g of freshly prepared 1-vinyl-6-methoxytetralol-1, 4 g of crystalline methylidihydroresorcinol, Triton B (from 0.8 g of trimethylbenzylammonium chloride, 0.24 g of potassium hydroxide, and 4 ml of alcohol), and 10 ml of xylene was heated for 45 minutes (in a flask with a water separator) at 130–140° in a current of nitrogen. The reaction mixture was cooled, diluted with 100 ml of ether, the unreacted methylidihydroresorcinol (1.1 g) was filtered off, the ether layer solution was washed three times with 5% potassium hydroxide solution and with water, and dried with magnesium sulfate. After filtration, distilling off the solvent, and crystallization, 5.0 g (50%) of 3-methoxy-8, 14-seco-D-homoestra-1,3,5,9-tetraen-14,17a dione (X) was obtained; m.p. 89–90° (from alcohol).

In one of the experiments the yield of the diketone was 52%. It was noted that use in the reaction of 1-vinyl-6-methoxytetralol-1 which had stood for several days (in a refrigerator) lowered the yield to 30%, and even less. Replacement of the xylene by dimethylformamide gave only 4% of the diketone (X).

Preparation of 3-methoxy-D-homoestra-1,3,5(10),8,14-pentaen-17a-one (I). Cyclization was carried out under the conditions previously described [1]. In one of the experiments 19 g (95%) of ketone (I) was obtained from 21.3 g of diketone (X).

Preparation of 19-nor-D-homoandrost-4-en-3,17a-dione (V). The starting ethylene ketal of 3-methoxy-D-homoestra-2,5(10)-dien-17a-one (IV) was prepared by the method described in [2]. To a heated solution of 130 mg of the ketal (IV) in 100 ml of glacial acetic acid was added 1 ml of hydrochloric acid (1:1), the mixture was heated to boiling, diluted with water, and the precipitate was filtered off. Yield 80 mg (74%) of 19-nor-D-homoandrost-4-en-3,17a-dione (V), m. p. 174–175° (from ethyl acetate);  $\lambda_{\max}$  (in alcohol) 230, 278  $\mu$ ;  $\log \epsilon$  3.98, 3.14; IR spectrum 1707, 1670  $\text{cm}^{-1}$ . Found: C 79.6, 79.7; H 9.0, 8.95%.  $\text{C}_{19}\text{H}_{26}\text{O}_2$ . Calculated: C 79.7; H 9.15%.

Synthesis of trans-D-homoequilenin (IX). A mixture of 400 mg of the diketone (X) and 10 g of dry, freshly prepared pyridine hydrochloride was heated for 40 minutes at 210–215° in a current of nitrogen. Upon cooling, the reaction product was treated, with stirring, with 200 ml of 5% potassium hydroxide solution, extracted with ether, and the aqueous solution was acidified to Congo. Crystals (230 mg) with m. p. 203–204° were separated, which after crystallization from alcohol melted at 234–235° and gave no depression in melting point with a known sample of trans-D-homoequilenin (IX);  $\lambda_{\max}$  230, 260, 270, 280.5, 292, 326, 339  $\mu$ ;  $\log \epsilon$  4.78, 3.58, 3.70, 3.75, 3.59, 3.33, 3.40. The acetate melted at 149–150°.

Isomerization of 3-methoxy-D-homoestra-1,3,5(10),8,14-pentaen-17a-one (I) to the methyl ether of trans-D-homoequilenin (VII). A mixture of 1 g of ketone (I), 10 ml of toluene, 10 ml of acetic acid, and 10 ml of concentrated hydrochloric acid was boiled for 4 hr in a current of nitrogen. The reaction mixture was extracted with toluene, the toluene solution was washed with 5% potassium hydroxide solution and with water and was dried with magnesium sulfate. After filtration, distillation of the solvent, and crystallization of the residue from benzene, 52 mg of the methyl ether of trans-D-homoequilenin (VII) was isolated with m. p. 210–212°, and which gave no depression in melting point with a known sample.

Ketalization of 3-methoxy-D-homoestra-1,3,5(10),8-tetraen-17a-one (II). A mixture of 10 g of ketone (II), 250 ml of toluene, 70 ml of ethylene glycol, and 0.5 g of p-toluenesulfonic acid was boiled while the toluene was slowly distilled off over the course of 8 hr (a total of 1 liter of toluene was distilled off). The reaction mixture was washed with a solution of sodium carbonate, then with water, the toluene solution was dried with magnesium sulfate, and the residue after distillation of the solvent was crystallized from ethyl acetate. Yield 4.6 g of ketal (III), m. p. 145–146°. From the mother liquors 0.45 g of the ethylene ketal of the methyl ether of trans-D-homoequilenin (VI) was separated, with m. p. 148–148.5° (from ethyl acetate);  $\lambda_{\max}$  (in alcohol) 228.5, 264.5, 287.5, 321, 336  $\mu$ ;  $\log \epsilon$  4.62, 4.01, 3.56, 3.13, 3.22. Found: C 77.7, 77.7; H 8.0, 8.0%.  $\text{C}_{22}\text{H}_{26}\text{O}_3$ . Calculated: C 78.1; H 7.7%. Furthermore, 120 mg of the methyl ether of trans-D-homoequilenin (IX) was obtained with m. p. 210–212°, giving no depression in melting point with a known sample.

Hydrolysis of the ethylene ketal of the methyl ether of trans-D-homoequilenin (VI). To a solution of 120 mg of ketal (VI) in 5 ml of acetic acid was added 1 ml of 1 N HCl, the mixture was heated to boiling, cooled, and diluted with water. After filtration and crystallization of the precipitate (m. p. 198–204°) from ethyl acetate, 50 mg



of the methyl ether of trans-D-homoequilenin (VII) was obtained with m. p. 211-212°, giving no depression with a known sample.

Isomerization of 3-methoxy-D-homoestra-1,3,5(10),8-tetraen-17a-one (II). A mixture of 370 mg of ketone (II), 5 ml of toluene, 5 ml of acetic acid, and 1 ml of hydrochloric acid was boiled for 2 hr. The reaction mixture was extracted with toluene, the toluene layer was washed with sodium carbonate solution and water, the solvent was distilled off in vacuum, and by crystallization of the residue from ethyl acetate 120 mg of material with m. p. 165-167° was obtained. By many crystallizations from ethyl acetate it was possible to isolate only the methyl ether of trans-D-homoequilenin with m. p. 200-203°, giving no depression in melting point with a known sample and having a UV spectrum which coincided with the spectrum of the known compound. Chromatography of the reaction products on alumina was not successful. When the hydrochloric acid was replaced by p-toluenesulfonic acid, the same complex mixture of products was obtained. The etherate of boron trifluoride at room temperature did not cause isomerization.

Preparation of the ethylene ketal of 3-methoxy-D-homoestra-1,3,5(10),8,14-pentaen-17a-one (XI). A mixture of 17 g of ketone (I), 120 ml of ethylene glycol, 0.6 g of p-toluenesulfonic acid, and 800 ml of toluene was refluxed for 6 hr with a condenser fitted with a water trap. After cooling the toluene was separated, the lower layer was extracted twice with ether, the combined extracts were washed with sodium bicarbonate solution, the solvents were distilled off in vacuum, and the residue was crystallized from alcohol. Yield 13.15 g (67%) of ketal (XI) with m. p. 117-119°. The pure ketal melted at 124-124.5°;  $\lambda_{\max}$  (in alcohol) 227, 307 m $\mu$ ; log  $\epsilon$  4.18, 4.48. Found: C 78.4, 78.5; H 7.8, 7.9%.  $C_{22}H_{26}O_3$ . Calculated: C 78.1; H 7.7%.

Hydrolysis of ketal (XI). Hydrolysis of ketal (XI) was carried out in a manner similar to the hydrolysis of ketal (IV). From 340 mg of ketal (XI) there was obtained (after crystallization from alcohol - ethyl acetate) 150 mg of ketone (I) with m. p. 134-136°, giving no depression in melting point with a known sample.

Hydrogenation of ketal (XI). Two grams of ketal (XI) in 20 ml of tetrahydrofuran was hydrogenated with palladium on calcium carbonate. In 2 hr 40 minutes 1 molecule of hydrogen was absorbed, the hydrogenation was stopped, the solution was filtered, the solvent was distilled off in vacuum, and the residue was crystallized from ethyl acetate. After the third crystallization 0.8 g of ketal (III) was obtained with m. p. 144-146°, giving no depression in melting point with a known sample.

Reduction of ketal (XI) by the Birch method. When the synthesis was carried out with a fivefold excess of lithium, 0.2 g of lithium was added to a solution (cooled to -40°) of 1 g of ketal (XI) in a mixture of 30 ml of dioxane, 50 ml of ether, and 150 ml of ammonia, and the mixture was stirred for 2 hr. The reaction mixture was decomposed with 5 g of dry ammonium chloride, the ammonia was removed, 200 ml of water was added, and extraction was carried out with chloroform. The extract was treated with carbon dioxide, washed with water, evaporated in vacuum, and after crystallization from ethyl acetate 0.4 g of ketal (III) was isolated with m. p. 135-138°, which after recrystallization melted at 142-143° and gave no depression in melting point with a known sample.

When the synthesis was carried out with a 35-fold excess of lithium in the presence of alcohol, 1.4 g of lithium was added to a solution (cooled to -40°) of 1 g of ketal (XI) in a mixture of 30 ml of dioxane, 50 ml of ether, and 150 ml of ammonia, and the mixture was stirred for 10 minutes, during which the solution darkened and a bronze-colored precipitate formed. Then 50 ml of absolute alcohol was added dropwise until the solution was decolorized, all the ammonia was removed by blowing dry nitrogen through, the mixture was decomposed (at -5°) with 270 ml of water and extracted with chloroform. The extract was washed with water, the solvent was distilled off, and the residue was crystallized from ethyl acetate. Yield 0.55 g of ketal (XII) with m. p. 109-114°. A second crystallization raised the melting point to 111-114°;  $\lambda_{\max}$  (in alcohol) 306 m $\mu$ ; log  $\epsilon$  1.88; IR spectrum (in  $CHCl_3$ ): 1669, 1696  $cm^{-1}$ . Found: C 76.9, 76.7; H 8.75, 8.5%.  $C_{22}H_{30}O_3$ . Calculated: C 77.15; H 8.8%.

Hydrolysis of ketal (XII). To a solution of 140 mg of ketal (XII) with m. p. 109-114° in 2 ml of acetic acid was added 0.75 ml of 1 N HCl, the solution was heated to boiling, cooled, poured into 50 ml of water, and extracted with chloroform. The extract was washed with sodium carbonate solution and with water, the solvent was distilled off, and the residue was crystallized from ethyl acetate. Yield 70 mg (60%) of 19-nor-D-homoandrost-4,8-dien-3,17a-dione (XIII) with m. p. 159-160°;  $\lambda_{\max}$  (in alcohol) 235 m $\mu$ ; log  $\epsilon$  4.30. Found: C 80.3, 80.2; H 8.8, 8.55%.  $C_{20}H_{26}O_2$ . Calculated: C 80.5; H 8.8%.

## SUMMARY

1. By the reduction of 3-methoxy-D-homoestra-1,3,5(10),8-tetraen-17a-one (III) with lithium and alcohol in liquid ammonia with subsequent hydrolysis, 19-nor-D-homoandrost-4-en-3,17a-dione (V) was obtained. A similar reduction of the ethylene ketal of 3-methoxy-D-homoestra-1,3,5(10),8,14-pentaen-17a-one (I) with a large excess of lithium led to 19-nor-D-homoandrosta-4,8-dien-3,17a-dione (XIII). Reduction of the ketal of (I) in the absence of alcohol gave ketal (III).

2. In acid medium 3-methoxy-D-homoestra-1,3,5(10),8-tetraen-17a-one (II) and its ketal (III) were partially dehydrogenated to the methyl ether of trans-D-homoequilenin (VII) or its ketal (VI); at the same time products were formed with a double bond in a different position than in ketone (I).

3. Under the conditions of demethylation 3-methoxy-D-homoestra-1,3,5(10),8,14-pentaen-17a-one (I) and 3-methoxy-8,14-seco-D-homoestra-1,3,5(10),9-tetraen-14,17a-dione (X) formed trans-D-homoequilenin (IX). Thus, starting from 6-methoxytetralone the synthesis of trans-D-homoequilenin was carried out in a total of three steps.

## LITERATURE CITED

1. S. N. Ananchenko and I. V. Torgov, Doklady Akad. Nauk SSSR 127, 553 (1959).
2. S. N. Ananchenko, V. N. Leonov, A. V. Platonova, and I. V. Torgov, Doklady Akad. Nauk SSSR 135, 73 (1960).
3. A. I. Wilds and N. A. Nelson, J. Amer. Chem. Soc. 75, 5366 (1953).
4. C. Djerassi, L. Miramontes, G. Rosenkranz, and F. Sondheimer, J. Amer. Chem. Soc. 76, 4092 (1954).
5. F. B. Colton, L. N. Nysted, B. Riegel, and A. L. Raymond, J. Amer. Chem. Soc. 79, 1123 (1957).
6. W. Dirscherl and F. Hanusch, Z. physiol. Chem. 233, 13 (1935); 236, 139 (1935); A. Serini and W. Logemann, Ber. 71, 186 (1938).
7. L. Fieser and M. Fieser, Chemistry of Natural Compounds of the Phenanthrene Series [Russian translation] (Goskhimizdat, Moscow - Leningrad, 1953) p. 187.
8. I. N. Nazarov, I. V. Torgov, and G. P. Verkholetova, Doklady Akad. Nauk SSSR 112, 1067 (1957).

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

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SYNTHESIS OF THE 2-ETHYLENEKETAL OF ANTI-TRANS-  
 $\Delta^{10}$ -DODECAHYDROPHENANTHRENETRIONE-2,5,8

K. K. Pivnitskii and I. V. Torgov

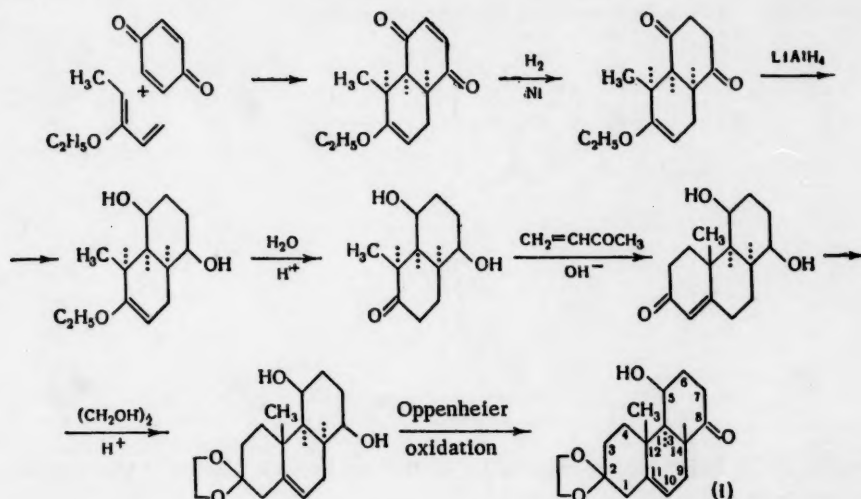
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No. 6, pp. 1080-1087, June, 1961

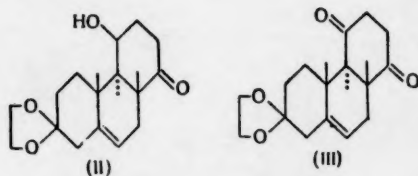
Original article submitted July 18, 1960

One of the best-known methods of synthesizing steroids with an oxygenous function at  $C_{11}$  is Sarett's synthesis [1]. In this synthesis of 2-ethyleneketal of anti-trans-12 $\beta$ -methyl- $\Delta^{10}$ -dodecahydrophenanthrenol-5 $\beta$ -dione-2,8 (I) serves as the key compound, obtained from 1-methyl-2-ethoxybutadiene-1,4 and benzoquinone by the following series of reactions [2]:



Furthermore, starting from this tricyclic ketol, Sarett synthesized cortisone and its isomers, while Wettstein and other Swiss and Dutch chemists have prepared aldosterone [3].

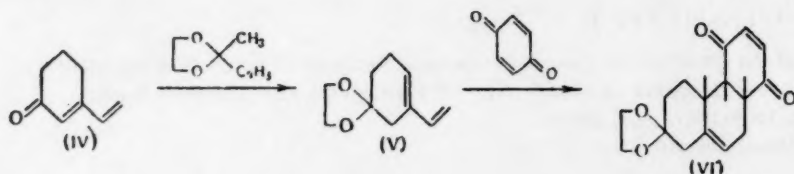
During the intensive study of the physiological properties of 19-norsteroids, great interest has been shown in preparation of the 12-noranalogue of ketol I (II) and the corresponding diketone (III) and their use in synthesis of 19-norcortisone, 19-noraldosterone and other steroids



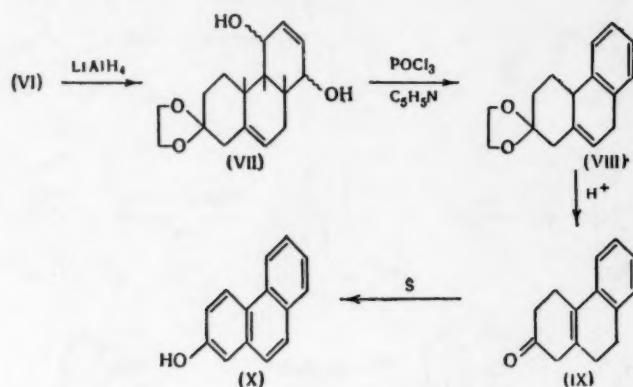
In the present work, synthesis is described of the 2-ethyleneketal of anti-trans- $\Delta^{10}$ -dodecahydrophenanthrenetri-  
 one-2,5,8 (III), starting from available benzoquinone and dehydroresorcine. 3-Vinyl- $\Delta^2$ -cyclohexenone (IV) is readily  
 prepared from the latter [4], and by reacting with 2-methyl-2-ethyldioxolane-1,3 [5] gave the ethyleneketal of 3-  
 vinyl- $\Delta^3$ -cyclohexenone (V).

Similar double bond migration in ketalization of  $\alpha, \beta$ -unsaturated ketones is the general rule in the  $\Delta^4$ -3-ketosteroid series [2, 6-8]. The structure of ketal (V) as a derivative of dienone (IV) with a transferred double bond was inferred from further conversions of it.

Diene ketal (V), unlike initial dienone (IV) [9], readily undergoes diene synthesis with *p*-benzoquinone, giving a good yield of adduct (VI)

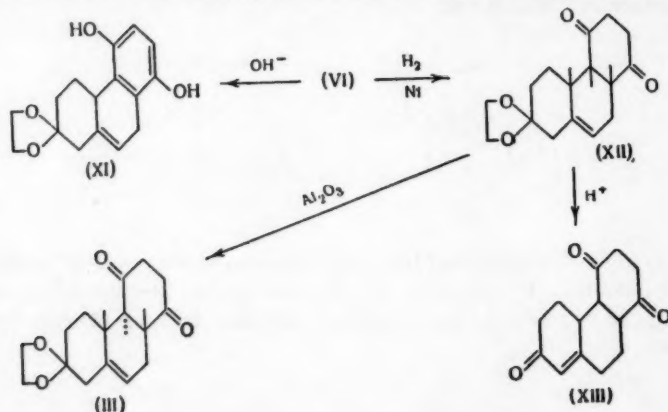


Syn-*cis*-configuration for adduct (VI) follows, as in the case of the adduct of  $\Delta^1$ -vinylcyclohexene with quinone also [10], from Alder's rules for diene synthesis [11]. The position of the ketal grouping, determining the structure of ketal (V), was proved in the following manner. On reducing adduct (VI) with lithium aluminumhydride [12, 13], unsaturated diol (VII) was obtained (evidently a mixture of epimers at C<sub>5</sub> and C<sub>8</sub> was formed). Diol (VII) was readily dehydrated by phosphorus oxychloride in pyridine into ethyleneketal (VIII), which, without purification, by treatment with *p*-toluenesulfonic acid was converted into tricyclic ketone (IX).



The position of the double bond in ketone (IX) was inferred from the absence of an absorption maximum in the u.v.-spectrum in the region 240 m $\mu$ .

Dehydrogenation of ketone (IX) with sulfur at 200° [14] led to 2-hydroxyphenanthrene, identical to the product obtained by counter synthesis consisting of sulfonation of phenanthrene and subsequent fusing with alkali [15]. The methyl ethers of the hydroxyphenanthrenes also appeared identical. Adduct (VI) is quite stable, but is readily aromatized to hydroquinone (XI) on treatment with aqueous alkali in dioxan and partially even on brief boiling in methanol. Boiling the adduct for half an hour in 1% pyridine solution in methanol also leads to complete aromatization.





Hydrogenation of adduct (VI) both over specially treated Raney nickel [16] and over palladium on strontium carbonate (in presence of triethylamine) leads to dihydro adduct (XII), to which is assigned the initial syn-cis-con-figuration, since the mild hydrogenation conditions exclude the possibility of isomerization [16]. The latter takes place on chromatography of syn-cis-dihydro adduct (XII) on alkaline aluminum oxide, isomer (III) thus formed possessing of necessity an anti-trans-configuration, this being thermodynamically more favorable for the diketododeca-hydrophenanthrene system [10]. This isomerization also proceeds with low yield on boiling dihydro adduct (XII) in 1% pyridine solution in methanol. Acid hydrolysis of ketal (XII) proceeds in a complex manner, giving a mixture of products, from which in low yield was isolated triketone (XIII) of undetermined configuration.

## EXPERIMENTAL

Melting points were determined in molybdenum glass capillaries rinsed with acid. In each case, drying of solutions was carried out with anhydrous magnesium sulfate, and evaporation — in vacuo. Ultraviolet spectra were determined in alcohol.

Ethyleneketal of 3-vinyl- $\Delta^3$ -cyclohexenone (V). 5.59 g of dienone (IV) [b. p. 77.3-79.0° (4 mm);  $n_D^{25}$  1.5438] [4] and 0.20 g of p-toluenesulfonic acid monohydrate were dissolved in 90 ml of 2-methyl-2-ethyldioxolane-1,3 (b. p. 115°), and 25 ml of distillate distilled from the solution in a current of nitrogen over a period of 3 hr, excess dioxolane then being removed in vacuo. The red-brown residue was dissolved in ether, the ethereal solution washed with soda solution, water, dried and evaporated.

On distilling the residue, 4.0 g (53%) of ketal (V) was obtained, b. p. 69-71° (0.5 mm);  $n_D^{22}$  1.5162. The analytical sample, obtained from a repeat distillation, took the form of a colorless oil with b. p. 78.0-78.5° (1 mm);  $n_D^{21}$  1.5166. Found: C 72.38, 72.27; H 8.53, 8.51%.  $C_{10}H_{14}O_2$ . Calculated: C 72.26; H 8.49%. On ketalizing dienone (IV) with ethylene glycol in benzene solution, yield of ketal (V) amounted to only 12.5%.

2-Ethyleneketal of syn-cis- $\Delta^{6,10}$ -decahydrophenanthrenetrione-2,5,8 (VI). A suspension of 2.08 g of freshly sublimated quinone in a solution of 3.76 g (17% excess) of ketal (IV) in 10 ml of dry ether was stirred continuously for 24 hr, mixed with the help of a glass-covered magnetic stirrer, then left for a week. The resulting crystals were filtered off and washed with a small amount of ether. 4.58 g (87%, calculated on quinone) of adduct (VI) was obtained with m. p. 168.0-169.7°. A sample with m. p. 165.5-167.0° from a similar experiment after two crystallizations from a benzene-hexane mixture took the form of light-yellow, wedge-shaped crystals with m. p. 164.8-166.0°;  $\lambda_{max}$  229, 292, 354 m $\mu$ ; log  $\epsilon$  4.02; 2.26; 1.82. Found: C 70.04, 70.11; H 6.42, 6.42%.  $C_{16}H_{18}O_4$ . Calculated: C 70.05; H 6.62%. In previous experiments, on crystallizing from methanol in presence of traces of pyridine a polymorphic modification of adduct (VI) was obtained as light-yellow plates with m. p. 154.5-155.0°,  $\lambda_{max}$  231.4; 290 m $\mu$ ; log  $\epsilon$  4.02; 2.26. Found: C 70.13, 70.13; H 6.57, 6.49%.  $C_{16}H_{18}O_4$ . Calculated: C 70.05; H 6.62%. A mixture of the modifications melted at 151.5-153.0°. On hydrogenation, both modifications gave the same product (see below). Repeated attempts to obtain this modification were unsuccessful.

2-Ethyleneketal of syn-cis- $\Delta^{6,10}$ -decahydrophenanthrenediol-5,8-one-2 (VII). A solution of 2.74 g of adduct (VI) in 50 ml of absolute ether and 70 ml of absolute dioxan were added dropwise to a suspension of 0.50 g of lithium alumohydride in 50 ml of absolute ether over a period of 1 hr. After stirring for 5 hr, the mixture was poured into 50 ml of saturated Seignette salt solution and 100 g of ice. The ethereal layer was separated, the aqueous extracted with chloroform; the united organic extracts were washed with saturated table salt solution and after drying, evaporated. The oily, brown residue was chromatographed on 100 g of aluminum oxide. On washing out with a benzene: chloroform (2: 8) mixture and with chloroform, two fractions were obtained (0.7 and 1.39 g, 25 and 50% respectively) of isomeric diols (VII) as a white, frothy mass. The i.r.-spectra of both fractions showed no carbonyl group absorption band. Found for the first fraction: C 69.27, 69.17; H 7.96, 8.06%; for the second fraction: C 69.40, 69.27; H 7.97, 7.87%.  $C_{16}H_{22}O_4$ . Calculated: C 69.03; H 7.97%

Conversion of diol (VII) into 2-hydroxyphenanthrene (X). To prepare 2-ethyleneketal- $\Delta^{5,7,10,13}$ -hexahydrophenanthrenone-2 (VIII), to a solution of 2.11 g of a mixture of diol (VII) fractions in 20 ml of absolute pyridine was added after 20 minutes in an atmosphere of dry nitrogen 5.2 ml of freshly distilled phosphorus oxychloride in 10 ml of absolute pyridine, maintaining the temperature within the range 17-22°. The mixture was stirred for 5 hr at 20°, 30 minutes at 80-85°, left for 12 hr and poured into 100 g of ice. The reaction products were extracted with ether and benzene, the extract washed twice with water and after drying and evaporation, 1.25 g (68%) of ketal (VIII) obtained as a light-yellow oil, which without purification was subjected to further conversion. To prepare  $\Delta^{5,7,11,13}$ -hexahydrophenanthrenone-2 (IX), a solution of 1.17 g of unpurified ketal (VIII) and 0.20 g of p-toluenesulfonic acid

monohydrate in 50 ml of acetone was left for 12 hr, diluted with 5% soda solution, extracted with ether, the ethereal solution washed with water until the aqueous layer was discolored. After drying the solution and evaporation of ether 1.02 g of a brownish oil remained, distillation of which resulted in 0.44 g (46%) of ketone (IX) as a light-yellow liquid with b. p. 135-155° (1 mm);  $\lambda_{\max}$  218.5, 225, 262.5, 267 m $\mu$ ; log  $\epsilon$  4.23, 4.18, 3.90, 3.89. To prepare 2-hydroxyphenanthrene (X), a mixture of 370 mg of ketone (IX) and 120 mg of finely ground sulfur was heated for 20 minutes at 190-210°; the temperature was raised to 240° over a period of 10 minutes, held at that temperature for 10 minutes, then for a further 7 minutes at 250°. Initially, rather vigorous hydrogen sulfide evolution occurred, ceasing toward the end. On cooling, the black fused product was dissolved by heating in 10 ml of 10% caustic soda, stirred with activated carbon, filtered, and the filtrate acidified with concentrated hydrochloric acid. The precipitate settling out was separated and dissolved in alcohol, filtered and precipitated with water. Using boiling water to which had been added 10% of alcohol, 78 mg (21%) of 2-hydroxyphenanthrene (X) with m. p. 162.5-164.5° was extracted from the precipitate. Successive crystallization from aqueous alcohol, water, and petroleum ether (b. p. 60-75°) increased the melting point to 167.4-168.0°. A sample mixed with authentic 2-hydroxyphenanthrene (m. p. 168.0-168.8°) had m. p. 167.4-168.0°, and the u.v.-spectra of both samples appeared identical. Methylation of the 2-hydroxyphenanthrene obtained led to the methyl ether, m. p. 96.6-97.0° (from aqueous methanol). A sample mixed with authentic 2-methoxyphenanthrene (m. p. 97.4-98.0°) melted at 97.0-97.6°. According to the data in literature, 2-hydroxyphenanthrene has m. p. 169°, the methyl ether, m. p. 100-101° [15].

2-Ethyleneketal of  $\Delta^{5,7,10,13}$ -hexahydrophenanthrenediol-5, 8-one-2 (XI). a) A suspension of 401 mg of adduct (VI) in 9 ml of methanol and 0.1 ml of pyridine was boiled in an atmosphere of nitrogen for 35 minutes, the homogeneous solution then evaporated in a stream of nitrogen; traces of pyridine were removed by distillation with benzene.

After crystallization from a mixture of benzene, ethanol, and hexane, the residue gave 321 mg (80%) of hydroquinone (XI) with m. p. 197-200° (with decomposition). By additional crystallization from a mixture of ethanol and benzene (with decolorization by activated carbon) an analytical sample was obtained as a cream-colored rhombohedra with m. p. 202.2-203.7°;  $\lambda_m$  292 m $\mu$ ; log  $\epsilon$  3.55. Found: C 69.79, 70.09; H 6.63, 6.66%.  $C_{16}H_{18}O_4$ . Calculated: C 70.05; H 6.62%. Sometimes hydroquinone (XI) crystallized as needles having a melting point identical to that of the rhombic form and giving no depression with it.

b) 438 ml of adduct (VI) was boiled for 6 minutes with 17 ml of methanol, the crystals dissolving completely toward the end. On cooling, 226.5 mg with m. p. 165.8-167.0° crystallized out, and after partial evaporation - a further 45 mg of crystals with m. p. 166-168°, identical with the initial adduct (VI) crystallized out; in all 271.5 mg (62%). By evaporating the mother liquor to dryness and recrystallizing from a mixture of acetone, benzene and hexane, 69.5 mg (15.9%) of hydroquinone (XI) was obtained as a modification with m.p. 182-183.5° [see the following experiment (c)]; a mixture with the high-melting modification from experiment (a) melted at 194-200.5°.

c) To a suspension of 413 mg of adduct (VI) in 7 ml of dioxan in an atmosphere of nitrogen with stirring at 20° were added 3.2 ml of 0.5 N caustic potash and 10 ml of water. The resulting red-brown solution was acidified by dropwise addition of dilute hydrochloric acid until it gave a strongly acidic reaction. The color of the solution changed to light-yellow, and after dilution with 17 ml of water 332 mg of hydroquinone (XI) with a double m. p. of 185.2° and 195.0-196.5° precipitated. By diluting the mother liquor with water a further 8 mg of a substance of comparable quality was obtained; total yield 82%. After crystallizing from a mixture of acetone and hexane, hydroquinone (XI) was obtained as small, thick sticks with a double m. p. 181-3° and 197-200.8°;  $\lambda_{\max}$  291.5 m $\mu$ ; log  $\epsilon$  3.59. This modification of hydroquinone (XI) on recrystallization from the same mixture with a seed of the high-melting modification was converted into the latter with m. p. 198.8-200.0°; a sample mixed with a sample from experiment (a) melted at 198.9-200.8°.

Diacetate of hydroquinone (XI). A solution of 94 mg of hydroquinone (XI) (m. p. 201.3-203.3°) in 1.4 ml of acetic anhydride and 1.4 ml of absolute pyridine was allowed to stand for four days at ~20°, then poured into water and extracted with benzene. The benzene extract was washed with saturated sodium bicarbonate solution, water, dried and evaporated. 105 mg (85%) of diacetate was obtained as pale crystals. After two recrystallizations from a mixture of benzene and petroleum ether (b. p. 60-75°), shining, colorless prisms were obtained with m. p. 170-173.5°. Found: C 67.07, 67.15; H 6.24, 6.20%.  $C_{20}H_{22}O_6$ . Calculated: C 67.02; H 6.19%.

2-Ethyleneketal of syn-cis- $\Delta^{10}$ -dodecahydrophenanthrenetrione-2,5,8 (XII). a) A solution of 4.22 g of adduct (IV) (m. p. 165-167°) in 275 ml of benzene was shaken in an atmosphere of hydrogen in presence of 4 teaspoonfuls

of specially treated Raney nickel [16]. Raney nickel lixiviated in the usual manner [17] was washed with alcohol, absolute alcohol, benzene, ethyl acetate, and kept under the latter for 3 weeks. After 5 minutes 1.11 of a hydrogen equivalent was absorbed and hydrogenation then ceased. The catalyst was filtered off through fibrous asbestos, and, after evaporation of the filtrate, the residue recrystallized from a mixture of benzene and petroleum ether (b. p. 60-75°). 3.24 g of diketone (XII) was obtained with m. p. 154.0-155.8°, a further 162 mg of (XII) with m. p. 150.0-153.5° being obtained from the mother liquor by crystallization from a mixture of benzene and ether; total yield 3.402 g (80%). An analytical sample was obtained by a repeat crystallization and sublimation at 140-160° (0.5 mm) as three-cornered plates with m. p. 155.5-157.0°. Found: C 69.73, 69.76; H 7.22, 7.24%.  $C_{16}H_{20}O_4$ . Calculated: C 69.54; H 7.30%. Similar hydrogenation of the low-melting modification of adduct (VI) (a sample with m. p. 148.5-149.8°) gave 70% of diketone (XII) with m. p. 151.5-155.0°, giving no melting point depression with the sample described above.

b) On hydrogenating 1.00 g of adduct (VI) in 70 ml of benzene over 0.30 g of 4% Pd/SrCO<sub>3</sub>, preliminarily saturated with hydrogen, in presence of 0.40 ml of triethylamine, after 40 minutes 1.29 of an equivalent of hydrogen was absorbed, hydrogenation then slowing down markedly and ceasing. After the usual treatment, 454 mg was obtained of diketone (XII) with m. p. 152-154° and 158.5 mg with m. p. 150-153°; total yield 60%. A sample of the main fraction mixed with a sample of diketone (XII) described above gave no depression.

2-Ethyleneketal of anti-trans- $\Delta^{10}$ -dodecahydrophenanthrenetrione-2,5,8 (III). a) A solution of 671 mg of diketone (XII) in 50 ml of benzene was absorbed on 50 g of commercial aluminum oxide (an aqueous extract had pH 8). After 20 hr storage, by washing out the column with 300 ml of a mixture of benzene and ether (7:3) 615 mg (92%) was obtained (after evaporation) of diketone (III) with m. p. 143.5-147.0°. After sublimation at 125-135° (1 mm) 106 mg of diketone gave 102 mg (96%) of white needles with m. p. 149.5-152.0°; in this manner, yield of purified diketone (III) amounted to 88%. A sample from a similar experiment, after recrystallization from a mixture of chloroform and ether, followed by sublimation, had m. p. 154.6-155.1°. A sample mixed with initial diketone (XII) melted at 126-140°. Found: C 69.85, 69.66; H 7.38, 7.65%.  $C_{16}H_{20}O_4$ . Calculated: C 69.54; H 7.30%.

b) A solution of 80 mg of diketone (XII) in 1.5 ml of methanol in presence of 1 drop of pyridine was boiled for 30 minutes, then diluted with an equal volume of water. On cooling, 6.5 mg (7.6%) of diketone (III) with m. p. 147.149° precipitated; a sample mixed with the sample described above melted at 147.5-149.5°.

$\Delta^{11}$ -Dodecahydrophenanthrenetrione-2,5,8 (XIII). A suspension of 326 mg of diketone (XII) in a mixture of 8 ml of 30% perchloric acid and 15 ml of tetrahydrofuran was stirred at room temperature for 10 minutes until completely dissolved and left for 3 hr 40 minutes. The yellow solution was poured into a mixture of 40 ml of saturated sodium bicarbonate solution and 100 ml of benzene. The aqueous layer was extracted twice with chloroform, the organic layers united, and after drying and evaporation the residue ground with a small amount of ether. Filtration gave 170 mg of a rose-colored powder with m. p. 152.0-158.5° (resinifying at 138°); in the filtrate was a red-brown oil. After crystallization from a small amount of acetone the solid product gave 56 mg of triketone (XIII) with m. p. 172-177°; from the mother liquor by crystallization from a mixture of acetone and ether at -70° a further 10 mg of triketone (XIII) was obtained with m. p. 169-173°; total yield 24%. By recrystallizing both portions of the crystals from benzene 50 mg (18.2%) was obtained with m. p. 183.0-183.5°. For analysis, triketone (XIII) was once again recrystallized and sublimed at 145-150° (0.25 mm). Small, white needles with m. p. 183.7-184.7° (with decomposition, in a sealed capillary) were obtained;  $\lambda_{\max}$  243.5 m $\mu$ ; log  $\epsilon$  4.13. Found: C 72.34, 72.29; H 6.90, 6.95%,  $C_{14}H_{16}O_3$ . Calculated: C 72.39; H 6.94%. Hydrolysis with hydrochloric acid in methanol or with p-toluene-sulfonic acid in acetone gave worse results.

With the aim of increasing yield the crude product obtained by hydrolysis of 442 mg of diketone (XII) in the manner described above, was chromatographed on 20 g of alkaline aluminum oxide (17 hr exposure before washing out). From the fraction (90 mg) washed out with mixtures of benzene and chloroform from 9:1 to 5:5, 51 mg (13.7%) of a stereoisomer of triketone (XIII) with m. p. 108-112° was obtained by grinding with ether. After recrystallization from a mixture of benzene and petroleum ether (b. p. 60-75°) and evaporative distillation at 140° (0.25 mm) a colorless oil was obtained which on grinding with ether crystallized completely, giving white crystals with m. p. 112-113°;  $\lambda_{\max}$  239 m $\mu$ ; log  $\epsilon$  4.16. Found: C 71.85, 71.86; H 6.99, 6.98%.  $C_{14}H_{16}O_3$ . Calculated: C 72.39; H 6.94%.

#### SUMMARY

1. Ketalization of 3-vinyl- $\Delta^2$ -cyclohexenone proceeds with shifting of the  $\alpha,\beta$ -double bond to the  $\beta,\gamma$ -position and with formation of the ethyleneketal of 3-vinyl- $\Delta^3$ -cyclohexenone (V).



2. Diene (V) readily reacts with quinone, giving the 2-ethyleneketal of syn-cis- $\Delta^{6,10}$ -decahydrophenanthrene-trione-2,5,8 (VI), the structure of which was proved by conversion into 2-hydroxyphenanthrene.

3. By successive hydrogenation and isomerization, from ketal (VI) the 2-ethyleneketal and anti-trans- $\Delta^{10}$ -dodecahydrophenanthrenetrione-2,5,8 (III) was obtained — a possible intermediate product in 19-norsteroid synthesis.

#### LITERATURE CITED

1. L. H. Sarett, G. E. Arth, R. M. Lukes, R. E. Beyler, G. I. Poos, W. F. Johns, and J. M. Constantín, J. Amer. Chem. Soc. **74**, 4974 (1952); G. E. Arth, G. I. Poos, and L. H. Sarett, J. Amer. Chem. Soc. **77**, 3834 (1955).
2. G. I. Poos, G. E. Arth, R. E. Beyler, and L. H. Sarett, J. Amer. Chem. Soc. **75**, 422 (1953).
3. J. Schmidlin, G. Anner, J. Billiter, K. Heusler, H. Ueberwasser, P. Wieland, and A. Wettstein, Helv. chim. acta **40**, 1034, 1438, 2291 (1957); A. Lardon, O. Schindler, and T. Reichstein, Helv. chim. acta **40**, 666 (1957); H. P. Uehlinger, C. Tamm, and T. Reichstein, Helv. chim. acta **40**, 2234 (1957); K. Heusler, P. Wieland, and A. Wettstein, Helv. chim. acta **41**, 997 (1958); **42**, 1586 (1959); W. J. van der Burg, D. A. van Dorp, O. Schindler, C. M. Slegmann, and S. A. Szpilfogel, Recueil. trav. chim. **77**, 171 (1958).
4. I. N. Nazarov, I. V. Torgov, and G. P. Verkholetova, Doklady Akad. Nauk SSSR **112**, 1067 (1957).
5. H. J. Dauben, Jr., B. Loken, and H. J. Ringold, J. Amer. Chem. Soc. **76**, 1359 (1954).
6. M. B. Fernholz, U. S. Patent 2378918, 1945; Chem. Abstrs. **39**, 5051 (1945).
7. R. Antonucci, S. Bernstein, R. Littell, K. J. Sax, and J. H. Williams, J. Organ. Chem. **17**, 1341 (1952); R. Antonucci, S. Bernstein, R. Lenhard, K. J. Sax, and J. H. Williams, J. Organ. Chem. **17**, 1369 (1952).
8. J. M. Constantín, A. C. Haven, Jr., and L. H. Sarett, J. Amer. Chem. Soc. **75**, 1716 (1953).
9. S. N. Ananchenko and I. V. Torgov, Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk **1960**, 1649.
10. P. A. Robins and J. Walker, J. Chem. Soc. **1954**, 3960.
11. K. Alder and G. Stein, Angew. Chemie **50**, 510 (1937).
12. R. B. Woodward, F. Sondheimer, D. Taub, K. Heusler, and W. M. McLamore, J. Amer. Chem. Soc. **74**, 4223 (1952).
13. W. Sandermann and K. Streisow, Chem. Ber. **90**, 693 (1957).
14. G. T. Tatevosyan and A. G. Vardanyan, Zhur. Obshchei Khim. **17**, 1528 (1947).
15. A. Werner, et al., Liebigs Ann. Chem. **321**, 248 (1902).
16. L. H. Sarett, R. M. Lukes, G. I. Poos, J. M. Robinson, R. E. Beyler, J. M. Vandegrift, and G. E. Arth, J. Amer. Chem. Soc. **74**, 1393 (1952).
17. Synthesis of Organic Compounds [in Russian- Vol. 3, IL, Moscow, 1949, p. 338.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. Some or all of this periodical literature may well be available in English translation. A complete list of the cover-to-cover English translations appears at the back of this issue.

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# INVESTIGATIONS INTO THE FIELD OF STEREOCHEMISTRY OF CYCLIC COMPOUNDS

## COMMUNICATION 39. SYNTHESIS AND STEREOSPECIFIC CONVERSIONS OF MONOESTERS OF CIS-SYN- AND CIS-ANTI- $\Delta^7$ -HYDRINDENE-4,5- DICARBOXYLIC ACIDS

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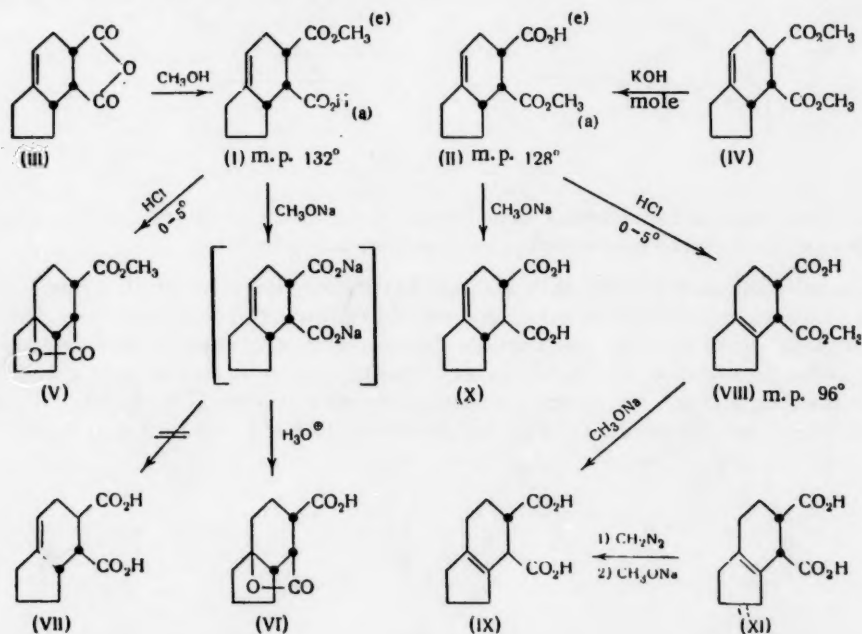
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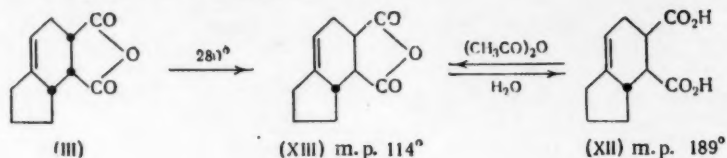
Continuing the previous work [1], we have investigated stereospecific conversions of the isomeric monoesters of cis-syn- $\Delta^7$ -hydrindene-4,5-dicarboxylic acid, for the preparation of which the stereoselective method developed previously [2] was used, based on the nonequivalence of the spatial character of the ortho-cis-carboxyl groups in the cyclic systems. The cis-syn-monoester (I) with an equatorial carbomethoxyl group at C<sub>5</sub> and the cis-syn-monoester (II) with an axial carbomethoxyl group at C<sub>4</sub> were prepared as the main reaction products: the first — by boiling cis-syn-anhydride (III) in methanol, the second — by partial saponification of cis-syn-diester (IV) with one mole of caustic potash in aqueous methanol. The structure and configuration of cis-syn-monoester (I) were verified by the following chemical conversions. It appeared that on reacting with dry hydrogen chloride under mild conditions (0-5°) this monoester is quantitatively converted into previously described cis-syn- $\gamma$ -lactoester (V) with an equatorial carbomethoxyl group at C<sub>5</sub>. Boiling monoester (I) with sodium methylate in the methanol resulted only in saponification of the carbomethoxyl group, and on acidification of the sodium salt obtained as an intermediate, only cis-syn- $\gamma$ -lactoacid (VI) was obtained, which, as was shown previously [1], is formed extremely readily from cis-syn- $\Delta^7$ -hydrindene-4,5-dicarboxylic acid even in a weakly acid medium. Formation of trans-syn- $\Delta^7$ -hydrindene-4,5-dicarboxylic acid (VII), theoretically possible in this reaction, was not observed.



The structure of monoester (II) follows from its inability to form a lactone. On reacting monoester (II) with hydrogen chloride under mild conditions, shift of the double bond to position 8,9 readily takes place, with formation of *cis*-monoester (VIII). The structure of the latter was in turn confirmed by the fact that, on reacting it with sodium methylate in methanol, previously described *trans*-dicarboxylic acid (IX) was obtained from it. Unlike its  $C_5$ -isomer monoester (II) is readily isomerized on boiling with sodium methylate, forming known *trans-anti*-dicarboxylic acid (X). All these conversions of monoester (II) fit in well with the structure ascribed to it. It should be noted that during attempt to prepare *cis*-monoester (VIII) or its  $C_5$ -isomer by saponification of the corresponding *cis*-diester with one mole of caustic potash in aqueous methanol, a liquid mixture of both the possible *cis*-monoesters was obtained. This points to the conformational instability of *cis*-acid (XI), as a result of which the two carbomethoxyl groups in the corresponding diester are practically equivalent spatially.

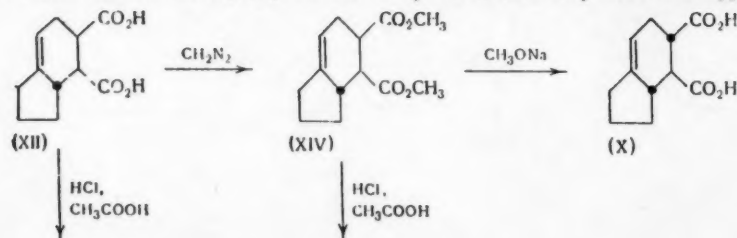
The inability of the carbomethoxyl groups at  $C_5$  in monoester (I) to isomerize with sodium methylate deserves special attention. Since there is no basis for ascribing to similar simple cyclic systems the existence of a reverse order of stability, it can be proposed that alkaline isomerization of the carbomethoxyl group, notwithstanding its equatorial disposition, must proceed with as a result of conversion of this monoester into the isomer with an axial carbomethoxyl group, as was observed in the case of its related  $C_2$ -monoester of *cis-syn*- $\Delta^4$ -octalin-1,2-dicarboxylic acid [3]. The fact that in the case of monoester (I) epimerization at  $C_5$  does not take place points to the rigidity of the  $\Delta^7$ -hydrindene-4,5-dicarboxylic acid system, this feature distinguishing it markedly from the corresponding octalin system. This fact affords additional confirmation of the correctness of the endostructure ascribed to initial *cis-syn*-anhydride (III). If this adduct has an *exo*-configuration, then *cis-anti*- $\Delta^7$ -hydrindene-4,5-dicarboxylic acid (XII) corresponding to it would not form a  $\gamma$ -lactone, not having been first converted into the other conversion form.

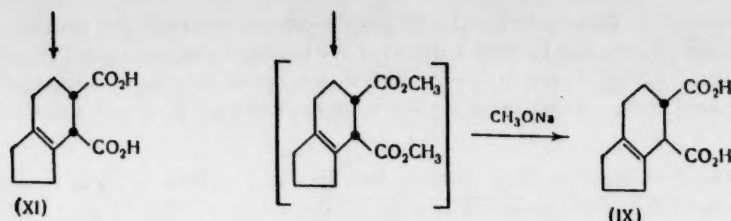
We achieved synthesis of this *cis-anti*- $\Delta^7$ -hydrindene-4,5-dicarboxylic acid (XII) and its derivatives (the configuration of which at  $C_9$  is opposite to that in the *syn-cis*-series), the main purpose being to verify whether conformational rigidity of the  $\Delta^7$ -hydrindene system occurred in this series also. *Cis-anti*-dicarboxylic acid (XII) and its anhydride (XIII) were prepared by thermal isomerization of *cis-syn*-anhydride (III). Similar thermal isomerization readily takes place in the case of the similar system — the anhydride of *cis-syn*- $\Delta^4$ -octalin-1,2-dicarboxylic acid, yield of *cis-anti*-anhydride exceeding 70% after boiling for 1 hr at 250° [4]. However, preparation of *cis-anti*-anhydride (XIII) is not possible under these conditions. Only on heating *cis-syn*-anhydride (III) at 280° is it possible to prepare *cis-anti*-anhydride (XIII), with a yield not exceeding 15-20%, saponification of which gives *cis-anti*-acid (XII). In addition, a 2-5% yield was obtained of the anhydride corresponding to *cis*-acid (XI), vigorous resinification occurring. Attempts to increase yield of products of the *cis-anti*-series by adding the thermal isomerization catalysts quinoline and diethylaniline were unsuccessful.



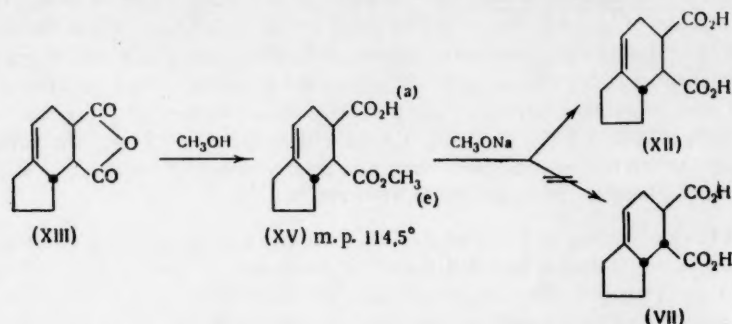
The difficulty associated with thermal isomerization of *cis-syn*-anhydride (III) permits the proposition that it possesses energy stability at least equivalent to that of *cis-anti*-anhydride (XIII).

The *cis-anti*-configuration of acid (XII) was proved by the following conversions. By the action of hydrogen chloride in acetic acid on acid (XII) the latter was converted into *cis*-dicarboxylic acid (XI), obtained previously in the *cis-syn*-series. Under the same conditions, the dimethyl ester (XIV) of the *cis-anti*-acid was converted, with subsequent alkaline isomerization, into *trans*-acid (IX). Finally, alkaline isomerization of diester (XIV) led to known *trans-anti*-dicarboxylic acid (X), also prepared previously in the *cis-syn*-series. From these conversions it follows that the differences between *cis-anti*-acid (XIII) and the *cis-syn*-acid stem only from their opposite  $C_9$  configuration.





Starting from the point proved previously [2], that alcoholysis of *cis*-anhydride ring leads predominantly to formation of an equatorial carbomethoxyl group, we ascribed an equatorial orientation to the carbomethoxyl group in *cis*-anti-monoester (XV), which was obtained as the sole product of boiling *cis*-anti-anhydride (XIII) with methanol.



On boiling this monoester with sodium methylate in methanol, only initial *cis*-anti-acid (XII) was obtained, i.e., instead of isomerization, only saponification of the equatorial carbomethoxyl group took place.

Thus, by alkaline isomerization both of *cis*-syn-monoester (I) and *cis*-anti-monoester (XV), possessing equatorial carbomethoxyl groups, we were unsuccessful in preparing the fourth theoretically possible *trans*-syn-isomer of  $\Delta^7$ -hydrindene-4,5-dicarboxylic acid. This points to the fact that, unlike the  $\Delta^4$ -octalin-1,2-dicarboxylic acid system, the  $\Delta^7$ -hydrindene-4,5-dicarboxylic acid system is not capable of a conversion entailing reversal of configuration of the substituents. However, such a conclusion needs further checking, since it was made on the assumption that the six-membered ring in all  $\Delta^7$ -hydrindene systems occurs with a half-chair conformation.

Absence of conversion in the hydrindene series indicates that the dimensions of the ring mainly depend on the flexibility of the bicyclic system. This also requires further confirmation.

#### EXPERIMENTAL

**Cis-syn-monoester (I).** A solution of 7.6 g *cis*-syn-anhydride (III) in 80 ml of absolute methanol was boiled for 6 hr, the methanol distilled off in vacuo, and the crystalline residue washed three times on a filter with absolute ether (in 10 ml lots). 4.9 g of *cis*-syn-monoester (I) was obtained with m. p. 124-128°. Recrystallization of the ester gave a pure sample which resolidified on melting at 126-128° and finally melted at 131-132°; yield 3.85 g. Found: C 64.30, 64.40; H 7.33, 7.10%; mole wt. 221.2 (by titration).  $C_{12}H_{16}O_4$ . Calculated: C 64.26; H 7.20%; mole wt. 224.25. By concentrating (by evaporation) the original ethereal mother liquor twice, a further 0.95 g of monoester (I) was obtained with m. p. 124-125°.

**Cis-syn-monoester (II).** To a solution of 1.6 g of caustic potash in 15 ml of water and 30 ml of methanol was added 6.3 g of *cis*-syn-diester (IV), and the mixture boiled for 3.5 hr. The methanol was distilled off in vacuo, the aqueous solution extracted with ether and acidified with hydrochloric acid (1:1). The resulting crystalline product was filtered off and washed with water. 5.25 g of *cis*-syn-monoester (II) was obtained with m. p. 122-124°. Recrystallization from ether gave 4.1 g of pure monoester (II) with m. p. 126.5-128°, which gave a marked depression when mixed with a sample of monoester (I). Found: C 63.96, 64.08; H 7.19, 7.14%; mole wt. 225.4 (by titration).  $C_{12}H_{16}O_4$ . Calculated: C 64.26; H 7.20%; mole wt. 224.25. From the ethereal extract after evaporation of solvent 0.5 g of initial *cis*-syn-diester (IV) was obtained.

Cis-syn- $\gamma$ -lactooester (V). Into a solution of 0.40 g of cis-syn-monoester (I) in a mixture of 10 ml of dioxan and 10 ml of ether, cooled to 0-5°, was bubbled a stream of dry hydrogen chloride. After 10 minutes the solvents were distilled off in vacuo. 0.38 g of crystals was obtained with m. p. 89-92°. Recrystallization from a mixture of ether and petroleum ether (1:2) gave pure cis-syn- $\gamma$ -lactooester (V) with m. p. 98-99°, identical with that described previously [1].

Attempt at alkaline isomerization of cis-syn-monoester (I). To a solution of 1 g of sodium in 20 ml of absolute methanol was added 0.9 g of cis-syn-monoester (I), and the resulting mixture boiled for 18 hr. The methanol was distilled off in vacuo, the residue dissolved in 30 ml of water, filtered, boiled for 2 hr, and again filtered with carbon. The aqueous solution was concentrated in a porcelain dish on a steam bath, the pasty precipitate of salts filtered from alkali, washed with absolute methanol and dissolved in the minimum volume of water. On acidifying with hydrochloric acid 0.70 g of crystals was obtained with m. p. 192-193°. After crystallization from water the substance had m. p. 196-197° and gave no depression with an authentic sample of cis-syn- $\gamma$ -lactooacid (VI).

Cis-monoester (VIII) and its conversion into trans-dicarboxylic acid (IX). a) Into a solution of 1.9 g of cis-syn-monoester (II) in a mixture of 15 ml of dioxan and 15 ml of ether, cooled, to 0-5° was bubbled a stream of dry hydrogen chloride. After 10 minutes the solvent was distilled off in vacuo; the liquid residue gradually crystallized. Yield of unpurified cis-monoester (VIII) with m. p. 89-92° amounted to 1.85 g. The crystals were purified by reprecipitation with water from an acetone solution. 1.35 g of pure cis-monoester (VIII) was obtained with m. p. 95-96°. Found: C 63.96, 63.97; H 7.31, 7.32%.  $C_{12}H_{16}O_4$ . Calculated: C 64.26; H 7.20%. The infrared spectrum of cis-monoester (VIII), taken in vaseline oil, indicated the presence of a carbomethoxyl group ( $\nu$  1742  $cm^{-1}$ ) and a carboxyl group with an intramolecular hydrogen bond ( $\nu$  1699  $cm^{-1}$ ).

b) To a solution of 1.2 g of sodium in 30 ml of absolute methanol was added 1.05 g of cis-monoester (VIII), and the mixture boiled for 18 hr. Methanol was distilled off in vacuo, the residue dissolved in 30 ml of water, filtered, boiled for 2 hr and again filtered. The aqueous solution was concentrated in a porcelain dish on a steam bath, the pasty precipitate of salts filtered from alkali, washed with absolute methanol and dissolved in the minimum volume of water. On acidification with hydrochloric acid 0.76 g of crystals was obtained with m. p. 155-157°. After crystallization from water, pure trans-acid (VIII) was obtained with m. p. 163-164°, giving no depression with an authentic sample of (I).

Trans-anti-dicarboxylic acid (X). To a solution of 0.8 g of sodium in 20 ml of absolute methanol was added 0.65 g of cis-syn-monoester (II), and the mixture boiled for 18 hr. Methanol was distilled off, in vacuo, and the residue treated in the manner described above. After acidification with hydrochloric acid 0.49 g was obtained of trans-anti-dicarboxylic acid (X) with m. p. 161-162°, giving no depression with an authentic sample of (I).

Cis-anti-dicarboxylic acid (XII). A mixture of 4.0 g of cis-syn-anhydride (III) and 0.1 g of pyrogallol was heated in an atmosphere of nitrogen at  $280 \pm 3^\circ$  for 90 minutes. After distillation in vacuo, a light-yellow oil was obtained with b. p. 160-162° (2.5 mm) and  $n_D^{20}$  1.526-1.530. To this product were added 3 ml of water and 3 ml of acetone, and the mixture boiled until a transparent solution resulted, after which water was added dropwise every 5 minutes until addition of water did not cause a further amount of turbidity. The solution was boiled for several minutes with activated carbon and filtered. On standing for 2-3 days crystals precipitated with m. p. 168-170°. After two crystallizations from aqueous acetone 0.80 g was obtained of pure cis-anti-dicarboxylic acid (XII) with constant m. p. 187.5-189°. Samples mixed with all the isomeric acids possible in this reaction gave depressions of the order of 10-15°. Found: C 62.60, 62.40; H 6.72, 6.53%; mole wt. 213.4 (by titration).  $C_{11}H_{14}O_4$ . Calculated: C 62.82; H 6.72%; mole wt. 210. From the mother liquors on concentration was obtained ~0.2 g of crystals with m. p. 158-164°, from which by crystallization from water was obtained 70 mg of cis-dicarboxylic acid (XI) with m. p. 179-181°.

Cis-anti-anhydride (XIII). A mixture of 0.57 g of cis-anti-acid (XII) and 5 ml of acetic anhydride was heated for 1 hr at  $90 \pm 1^\circ$  and allowed to stand at room temperature for 24 hr. After distillation of volatile products in vacuo, the solid residue was dissolved in ether and filtered from polymeric impurities. Ether was distilled off and 0.50 g of crystals obtained with m. p. 104-107°. After crystallization from an ether-hexane mixture (3:1), 0.42 g was obtained of pure cis-anti-anhydride with constant m. p. 113-114°. The infrared spectrum of anhydride (XIII) indicated the absence of a conjugated double bond and an anhydride ring. Found: C 68.38, 68.43; H 6.32, 6.17%.  $C_{11}H_{12}O_3$ . Calculated: C 68.72; H 6.30%. By saponifying anti-cis-anhydride (XIII) in aqueous-acetone solution, initial cis-anti-acid (XII) was readily formed.



Cis-anti-diester (XIV). A solution of 1.25 g of cis-anti-dicarboxylic acid (XII) in 2 ml of methanol was treated with excess ethereal diazomethane solution and the solvents distilled off. The residue was distilled in vacuo and 1.15 g obtained of cis-anti-diester (XIV) with b. p. 147-149° (7.5 mm) and  $n_D^{20}$  1.4940. Found: C 65.30, 65.26; H 7.44, 7.46%.  $C_{13}H_{18}O_4$ . Calculated: C 65.51; H 7.61%.

Conversion of cis-anti-dicarboxylic acid (XII) and its diester (XIV). a) To 0.40 g of cis-anti-acid (XII) was added 5 ml of saturated hydrogen chloride solution in glacial acetic acid, and the mixture heated at  $70 \pm 1^\circ$  for 90 minutes. Volatile products were distilled off in vacuo, and the solid residue (0.3 g) washed on a filter with a small amount of ether. A product was obtained with m. p. 145-155°, containing no halogen, and from which after three crystallizations from water was obtained 0.12 g of pure cis-acid (XI) with m. p. 180-182°, identical with an authentic sample of (I). A sample mixed with the initial acid gave a sharp depression.

b) To 0.70 g of cis-anti-diester (XIV) was added 7 ml of hydrogen chloride solution in glacial acetic acid, and the mixture heated at  $70 \pm 1^\circ$  for 90 minutes. Volatile products were distilled off under low vacuum, and to the residue added a solution of 0.8 g of sodium in 20 ml of absolute methanol. After boiling for 18 hr, methanol was distilled off, and the residue treated in a manner described for alkaline isomerization of monoesters (I), (II), and (VIII). After acidification, 0.35 g was obtained of crystals with m. p. 145-147°. After two crystallizations from water, 0.17 g was obtained of crystals of trans-acid (IX) with m. p. 163-165°.

c) To a solution of 0.5 g of sodium in 15 ml of absolute methanol was added 0.30 g of cis-anti-diester (XIV), and the mixture boiled for 18 hr. After distillation of methanol and treatment of the residue in the manner described above, 0.17 g was obtained of trans-anti-dicarboxylic acid (X) with m. p. 161-163°, identical with an authentic sample.\*

Cis-anti-monoester (XV). A solution of 0.45 g of cis-anti-anhydride (XIII) in 15 ml of absolute methanol was boiled for 8 hr. The solvent was distilled off in vacuo and a light-yellow, rapidly crystallizing oil obtained. After crystallization from an ether-hexane mixture (2:1), 0.39 g was obtained of cis-anti-monoester (XV) with constant m. p. 113-114.5°. Found: C 64.41, 64.39; H 7.06, 6.98%; mole wt. 228.3 (by titration).  $C_{12}H_{16}O_4$ . Calculated: C 64.26; H 7.20%; mole wt. 224.25.

Attempt at alkaline isomerization of cis-anti-monoester (XV). To a solution of 0.8 g of sodium in 25 ml of absolute methanol was added 0.40 g of cis-anti-monoester (XV), and the mixture boiled for 18 hr. Methanol was distilled off in vacuo, the residue saponified by boiling with 10 ml of water, the aqueous solution concentrated on a steam bath until a paste of salts formed, which was pressed out and washed with absolute methanol. The saturated aqueous salt solution was acidified with hydrochloric acid and 0.26 g obtained of crystals with m. p. 179-181°. After crystallization from water, 0.20 g was obtained of pure cis-anti-acid (XII) with m. p. 187-188°, which gave no depression with an authentic sample.

#### SUMMARY

1. Synthesis was achieved and structure proved for both monoesters of cis-syn- $\Delta^7$ -hydrindene-4,5-dicarboxylic acid.
2. Cis-anti- $\Delta^7$ -hydrindene-4,5-dicarboxylic acid was prepared and its configuration proved. Formation of cis-anti-anhydride (XIII) on thermal isomerization of cis-syn-anhydride (III) takes place with much greater difficulty than similar conversion in the octalin series.
3. The results obtained on alkaline isomerization of cis-syn-monoester (I) and cis-anti-monoester (XV) indicate a greater conformational rigidity for the  $\Delta^7$ -hydrindene-4,5-dicarboxylic acid system compared with the corresponding octalin system.

#### LITERATURE CITED

1. V. F. Kucherov and E. P. Serebryakov, *Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk* **1960**, 1057.
2. I. N. Nazarov and V. F. Kucherov, *Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk* **1954**, 63.
3. I. N. Nazarov, V. F. Kucherov, and V. M. Andreev, *Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk* **1956**, 817.
4. I. N. Nazarov, V. F. Kucherov, and V. M. Andreev, *Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk* **1956**, 715.

\* In other cases, on acidification a hydrate was formed with m. p. 76-78°; it could be dried by dissolving in benzene with subsequent azeotropic distillation.

# THE ALKYLATION OF PHENOLS BY COMPOUNDS WITH MIXED FUNCTIONS

## COMMUNICATION 1. THE ALKENYLATION OF m-CRESOL BY ALLYL ALCOHOL

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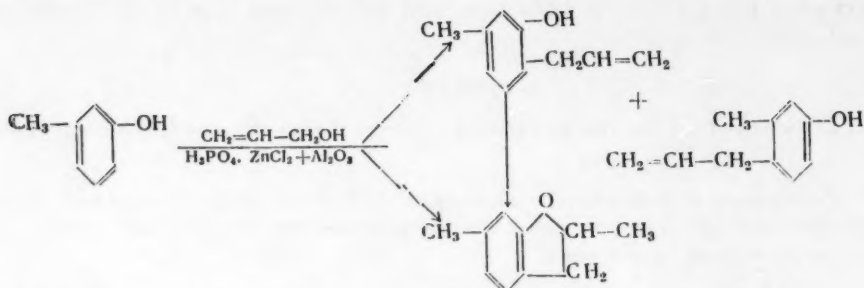
Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*,

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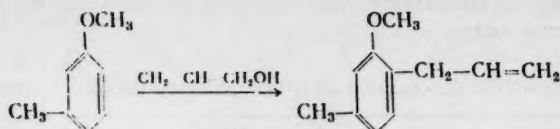
Original article submitted April 19, 1960

The alkenylphenols are of considerable interest as antioxidants, and also as starting products for the preparation of elastic materials and insecticides. However a description of their synthesis by the alkenylation of phenols by unsaturated alcohols has thus far been limited to the work of Niederl [1], Chichibabin [2], Losev [3] and co-workers. Niederl [1] has reported that he separated 3-methyl-6-isopropenylphenol in good yield from the products of the alkenylation of m-cresol by allyl alcohol in the presence of sulfuric acid in the cold. Later, Losev, Smirnova and Ryadneva [3] reported that on alkenylating phenol by allyl alcohol under these conditions they only obtained a tar from which they were unable to separate individual constituents by fractional distillation. Chichibabin [2] used phosphoric acid in the alkenylation of phenol by allyl alcohol. He obtained a substituted phenol to which he ascribed the propenylphenol structure. Losev, Smirnova and Ryadneva [3], who carried out the reaction at 70°, believe that they separated out o-isopropenylphenol, with a small admixture of the para isomer. However in the papers of Chichibabin [2] and Losev [3] no evidence is presented to show the structure of the phenols which they prepared.

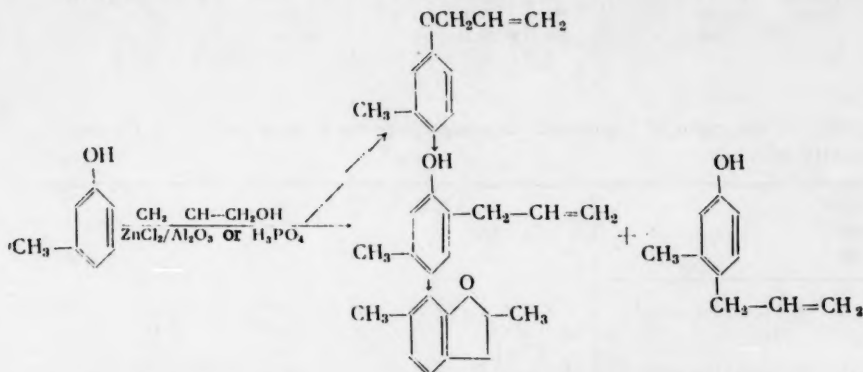
We studied the alkenylation of m-cresol by allyl alcohol in the presence of a number of acid catalysts: phosphoric acid, zinc chloride deposited on aluminum oxide, and cationite KU-1 which is a sulfonated phenol-formaldehyde resin activated by hydrochloric acid. In all the experiments with phosphoric acid and zinc chloride deposited on aluminum oxide that were carried out at 150 and 175°, allyl-m-cresol was obtained as the ortho- and para-isomers. The neutral reaction products were 2,6-dimethylcoumaran:



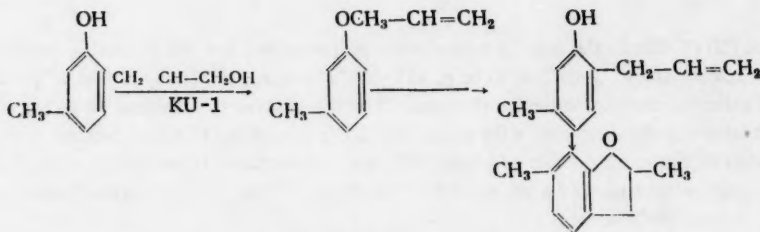
On alkenylation of m-cresol by allyl alcohol in the presence of KU-1 at a temperature of 95°, we only obtained 3-methyl-6-allylphenol. In the neutral fraction of the products of catalysis, besides 2,6-dimethylcoumaran, the allyl ether of m-cresol was detected. The structure of the allyl-m-cresols was determined by preparing phenoxy derivatives of the methyl ethers, and also by the oxidation of the latter to the corresponding methoxyphthalic acids. The structure of the radical in allyl-m-cresol was demonstrated by the hydrogenation of 3-methyl-6-allylphenol to 3-methyl-6-n-propylphenol. In addition we carried out an independent synthesis of 3-methyl-6-allylphenol by the rearrangement of the allyl ether of m-cresol. As was shown in one of the papers [4], using the allyl ether of phenol as an example, this rearrangement is not accompanied by isomerization of the radical, which was determined by the use of labeled atoms. In order to explain the reaction mechanism, we carried out the alkenylation of the methyl ether of m-cresol by allyl alcohol in the presence of phosphoric acid at 75°:



In this case the course of the reaction is such that the intermediate formation of an ether is excluded. Inasmuch as no para isomer is formed during the rearrangement of the ether under the conditions we used, although it does occur on the direct alkenylation of m-cresol, one may assume that the reaction goes simultaneously in two directions: by means of C-alkenylation and O-alkenylation. Meanwhile the O-alkenylation product becomes rearranged to the ortho isomer with subsequent cyclization to 2,6-dimethylcoumaran. Favorable to the acceptance of such a mechanism is the fact that, on rearrangement of the allyl ether of m-cresol, there is formed, as the principal product of cyclization, a product which is identical with the diethylcoumaran which is separated from the products of direct alkenylation:



The absence of the para isomer and the presence of a considerable quantity of the allyl ether of m-cresol among the products of catalysis in the experiment with KU-1, permits one to assume that direct alkenylation of the nucleus did not occur in this case.



#### EXPERIMENTAL

The original m-cresol boiled at  $86-87^\circ$  (10 mm) and had  $n_D^{20}$  1.5390 and  $d_4^{20}$  1.0334. Allyl alcohol: b. p.  $95-96^\circ$  (760 mm);  $n_D^{20}$  1.4136 and  $d_4^{20}$  0.8578.

The following were tried as catalysts: zinc chloride (20%) deposited on aluminum oxide, commercial ortho-phosphoric acid, sp. gr., 1.74, and cationite KU-1. The alkenylation of m-cresol by allyl alcohol in the presence of zinc chloride deposited on aluminum oxide, was carried out in an electrically heated rocking autoclave. The reactions in the presence of phosphoric acid and of KU-1 were carried out in a flask equipped with a mechanical stirrer, a reflux condenser, a thermometer and a dropping funnel.

The results of the experiments on alkenylating m-cresol in the presence of these catalysts are shown in Table 1. In all the experiments the original reagents were taken in equimolecular ratios. On the completion of each experiment the products of catalysts were separated from the catalyst and divided into phenolic and neutral fractions by treatment with a 10% solution of caustic soda. Table 2 shows the properties of the substances we separated, which

were obtained in experiments with the different catalysts. The phenolic fraction of the products of catalysis was a mixture of the isomers of allyl-m-cresols.

TABLE 1. Results of the Experiments on Alkenylating m-Cresol by Allyl Alcohol

Catalyst	Quantity of catalyst in % of wt. of reactants	Temp., °C	Length of expt., hrs.	Yield of catalyst in % of wt. of reactants	Total yield of alkenylation prods.		Yield of neutral prods. as % of cresol reacted				Yield of allyl-m-cresols (based on m-cresol reacted)	
					% of theoret.	% of m-cresol reacted	total yield	allyl ether of m-cresol	2,6-di-methyl-coumaran	o-isomer	p-isomer	
ZnCl <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	10	100	8	95,0	5,7	19	16,2	3	13,2	2,8		
Same	10	150	8	93,5	22,0	62,6	16,6	0,5	16,0	20,0	26,0	
»	10	175	8	91,8	47,0	71,6	26,6	Trace	26,6	14,0	31,6	
H <sub>3</sub> PO <sub>4</sub>	200	75	8	94,2	45,0	70,4	3,8	—	3,8	37,6	27,0	
Same	100	75	8	91,0	27,0	66,6	3,3	—	3,3	33,3	30,0	
»	100	95	8	89,0	39,0	61	17	—	17,0	23,0	21,1	
KU-1	20	95	12	73,0	7,5	53,5	31	20,0	11,0	22,5	—	

TABLE 2. Properties of Compounds Separated from the Alkenylation of m-Cresol by Allyl Alcohol

No. of compound	Name	Catalyst	B. p. °C at 10 mm	n <sub>D</sub> <sup>20</sup>	d <sub>4</sub> <sup>20</sup>	MR	M.p. of phenoxy derivative, °C
I	3-Methyl-6-allyl-phenol	ZnCl <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	106—108	1,5415	1,0199	45,66	87—88
		H <sub>3</sub> PO <sub>4</sub>	107—108,5	1,5424	1,0205	45,62	87—87,5
		KU-1	105—107	1,5420	1,0202	45,66	87—88
II	3-Methyl-4-allyl-phenol	ZnCl <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	122—124	1,5432	1,0212	45,69	111—112,5
		H <sub>3</sub> PO <sub>4</sub>	123—124	1,5430	1,0214	45,69	112—113
III	Allyl ether of m-cresol	KU-1	84—85	1,5203	0,9582	45,95	—
IV	2,6-Dimethyl-coumaran	ZnCl <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	91,5	1,5280	1,0082	45,19	—
		H <sub>3</sub> PO <sub>4</sub>	91—92	1,5279	1,0082	45,16	—
		KU-1	92—93	1,5300	1,0092	45,32	—

For phenols (I) and (II) (Table 2) the methyl ethers were prepared and had the following properties: a) b. p. 107-109° (14 mm); n<sub>D</sub><sup>20</sup> 1.5282 and d<sub>4</sub><sup>20</sup> 0.9724; b) b. p. 115-117° (14 mm); n<sub>D</sub><sup>20</sup> 1.5278 and d<sub>4</sub><sup>20</sup> 0.9742. By the oxidation of the methyl ethers according to the method described by Karavaev, Bashkurov and Kraeva [5], 3-methoxyterephthalic acid was obtained in the first case with m. p. 273-274°; according to the literature it melts at 274° [5]. From the oxidation product of the methyl ether of phenol (II), 4-methoxyphthalic acid with m. p. 158-160° was separated; the same literature source showed a m. p. of 160° for it [5]. Thus, phenol (I) (see Table 2) is o-allyl-m-cresol, while phenol (II) is p-allyl-m-cresol.

Phenoxy derivatives were prepared from both of the allyl cresols. The melting point of the phenoxy derivative of 3-methyl-4-allylphenol (II) is 112-113° and corresponds with the value 113° given in the literature [6]. The melting point of the phenoxy derivative of 3-methyl-6-allylphenol (I) of 87-88° corresponds with the melting point of the phenoxy derivative of o-allyl-m-cresol prepared by the alkylation of m-cresol by allyl chloride [6], to which the authors, apparently, erroneously ascribe the structure of 3-methyl-2-allylphenol.

The hydrogenation of 3-methyl-6-allylphenol was carried out in an alcohol solution in the presence of Raney nickel at 40-42°. Nine g of 3-methyl-6-n-propylphenol, b. p. 112-113° (12 mm); n<sub>D</sub><sup>20</sup> 1.5265 and d<sub>4</sub><sup>20</sup> 1.0016 was obtained from 15 g of 3-methyl-6-allylphenol. For 3-methyl-6-n-propylphenol the literature shows b. p. 115-117° (13 mm); n<sub>D</sub><sup>20</sup> 1.5261 [6].

Rearrangement of the allyl ether of m-cresol. The allyl ether of m-cresol was prepared by the method of Claisen [7]; its properties were — b. p. 84-85° (10 mm); n<sub>D</sub><sup>20</sup> 1.5185 and d<sub>4</sub><sup>20</sup> 0.9625 and correspond with those shown in the literature [8]. In order to carry out the rearrangement, 28 g of the allyl ether of m-cresol was mixed with



50 g of orthophosphoric acid and heated at 75° for eight hours. From this 18 g of 2,6-dimethylcoumaran, b. p. 92-93° (10 mm);  $n_D^{20}$  1.5278 and  $d_4^{20}$  1.0084, and 0.5 g of 3-methyl-6-allylphenol, b. p. 105-108° (10 mm);  $n_D^{20}$  1.5422. The remaining fraction of the products of catalysis consisted of a polymerization product and tarry material.

The alkenylation of 3-methylanisole. 3-Methylanisole was prepared by the Gattermann method [9]; m. p. 175-176° (760 mm);  $n_D^{20}$  1.5169 and  $d_4^{20}$  0.9720. Forty g (0.33 M) of 3-methylanisole was mixed with 100 g (1 g mole) of orthophosphoric acid; to this mixture, which was warmed to 75°, was gradually added 19 g (0.33 M) of allyl alcohol over the course of two hours. The reaction yielded 6 g of the methyl ether of 3-methyl-6-allylphenol, b. p. 105-107° (14 mm);  $n_D^{20}$  1.5269 and  $d_4^{20}$  0.9760. By oxidizing it according to the method described by Karavaev, Bashkurov and Kraeva [5], 3-methoxyterephthalic acid, m. p. 273-274° was obtained. The neutral fraction of the products of catalysis in all cases (see Table 2) was 2,6-dimethylcoumaran, b. p. 91.5° (10 mm);  $n_D^{20}$  1.5280;  $d_4^{20}$  1.0082. The properties of this 2,6-dimethylcoumaran correspond with the properties of dimethylcoumaran which we prepared by the rearrangement of the allyl ether of m-cresol. On alkenylating m-cresol by allyl alcohol over KU-1 a fraction was obtained - b. p. 84-85° (10 mm);  $n_D^{20}$  1.5203;  $d_4^{20}$  0.9582, whose properties were close to those of the product we synthesized from the allyl ether of m-cresol (see above).

#### SUMMARY

1. As a result of a study of the alkenylation of m-cresol by allyl alcohol in the presence of acid catalysts - phosphoric acid, zinc chloride deposited on aluminum oxide, and cationite KU-1, conditions were found which gave a yield of products of alkenylation that reached 47% of the theoretical.
2. The reaction products are isomeric allyl-m-cresols and 2,6-dimethylcoumaran.
3. The reaction mechanism of the alkenylation of m-cresol by allyl alcohol was explained.

#### LITERATURE CITED

1. J. B. Niederl, R. A. Smith, and M. E. McGreal, J. Amer. Chem. Soc., **53**, 3390 (1931).
2. A. E. Chichibabin, Izv. AN SSSR, OMEN, **1935**, 951.
3. L. P. Losev, O. V. Smirnova, and L. P. Ryadneva, Zb. statei po obshchei khimii, Izv. AN SSSR, M. **1**, p. 548 (1953).
4. H. Schmid and K. Schmid, Helv. chim. Acta **35**, 1879 (1952).
5. N. M. Karavaev, A. N. Bashkurov, and L. P. Kraeva, Khimia tverdogo topliva **6**, 585 (1933).
6. I. L. Kotlyarevskii, A. A. Samoilova, and N. A. Sherina, Izv. sib. otd. AN SSSR, No. 6, 54 (1958).
7. L. Claisen, Liebigs Ann. Chem. **418**, 78 (1918).
8. V. I. Pensevich-Kolyada and Z. B. Idel'chik, Zh. obshch. khimii **25**, 2215 (1955).
9. L. Gatterman and G. Viland, Prakticheskie raboty po organicheskoi khimii, Goskhimizdat, M. (1948), p. 281.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. Some or all of this periodical literature may well be available in English translation. A complete list of the cover-to-cover English translations appears at the back of this issue.

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# CATALYTIC ALKYLATION OF TETRALIN

## COMMUNICATION 5. ALKYLATION OF TETRALIN BY PRIMARY ALCOHOLS CONTAINING C<sub>7</sub> AND ABOVE

N. I. Shulkin, N. A. Pozdnyak, and E. D. Lubuzh

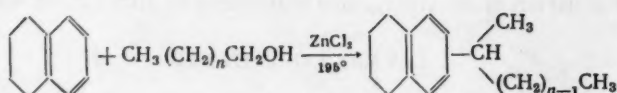
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No. 6, pp. 1098-1102, June, 1961

Original article submitted June 30, 1960

Recently we showed that the alkylation of tetralin by nonanol-1 takes place in the liquid phase in the presence of zinc chloride at 195-200° and at atmospheric pressure [1]. Under these conditions the yield of the nonyl-tetralin fraction boiling at 190-200° (9 mm) amounts to ~50% calculated on the tetralin and alcohol, and to ~70% calculated on the tetralin that actually reacts. In the present work we studied the alkylation of tetralin by primary alcohols of normal structure: heptyl, decyl and dodecyl. The experiments were carried out under the conditions which we had previously found to be optimal.



The yields of heptyl, decyl and dodecyltetralins amounted to 49.5, 48.3 and 38.5% respectively, calculated on the alcohol, and to 49.5, 48.3 and 19.4% calculated on the tetralin used. The yields based on tetralin that actually reacted amounted to ~70% in all cases. In the present paper data are presented on the structure of the alkyltetralins prepared both in the present study, as well as in earlier ones [1, 2]. A method of determining the structure of alkyltetralins was described by us in a separate article [3].

## EXPERIMENTAL

A mixture of tetralin, alcohol and zinc chloride in molar ratios (0.5 M), was heated for five hours at 195°. The reaction mixture was freed from zinc chloride, dried over calcium chloride, and distilled through a column with an effectiveness of 15 theoretical plates. The alkene, tetralin and alkyltetralin fractions were separated. Results of typical experiments are shown in Table 1. The analysis of the alkene fractions was carried out by the aid of combination dispersion spectra.\* The composition of the alkyltetralin fractions was determined by infrared spectroscopy. The infrared spectra were taken on an IKS-12 spectrophotometer with an NaCl and LiF prism. In order to determine the position of the alkyl group, infrared spectra of the alkyltetralin fractions were taken in the 700-850 cm<sup>-1</sup> and 1600-2000 cm<sup>-1</sup> regions, since it is known that in these regions nonplanar deformation vibrations of the C-H bonds of the aromatic ring and their overtones are observed [4]. Spectra in the region of the C-H valence vibrations at 2800-3000 cm<sup>-1</sup> were taken in order to determine the structure of the alkyl group. The intensity of the 2930 and 2960 cm<sup>-1</sup> bands of the corresponding unsymmetrical valence vibrations of the C-H bonds in the CH<sub>2</sub> and CH<sub>3</sub> groups were studied. It was shown previously [3, 5] that the extinction coefficient  $\epsilon_2$  of the 2960 cm<sup>-1</sup> band increases in proportion to the number of CH<sub>3</sub> groups in alkanes, alkylbenzenes and alkyltetralins (1 CH<sub>3</sub> group per ~100 units). The extinction coefficient  $\epsilon_1$  of the 2930 cm<sup>-1</sup> band, beginning with the propyl radical, also shows a proportional relationship to the number of CH<sub>2</sub> groups. For the alkyltetralins  $\epsilon_1 = 73n_1 - 120$  [3]. By means of this relationship, the total number of CH<sub>3</sub> groups  $n_1$  in alkyltetralin can be determined, and thus also the number of CH<sub>2</sub> groups in the alkyl radical.

From the data shown in Table 1 it is evident that on alkylating tetralin by means of alcohols, the corresponding fractions of alkenes (I, V and XI) are separated. Analysis by means of combination dispersion spectra showed that fraction I, b. p. 90-95°, was a mixture consisting of heptene-1 and heptene-2, principally the trans-isomers.

\*Raman Spectra.

The decene fraction V, which boiled within the limits of 35-45° (4.5 mm), consisted of decene-5 (trans-isomer) and a small quantity of decene-1. Analysis of fraction XI, b. p. 75-80° (4.5 mm) showed that it consisted of a mixture of tetralin and dodecene with a double bond located in the middle of the molecule. Fractions II, VI and X consisted basically of tetralin that had not reacted. The decreased index of refraction of fraction X is explained by the presence of dodecene, since the latter has a boiling point close to that of tetralin. Infrared spectroscopic analysis and comparison of physical properties of the intermediate fraction VII only succeeded in establishing the presence of a small quantity of decyl alcohol. Fraction XII corresponds with dodecyl alcohol, characterized by an infrared absorption band at 3350 cm<sup>-1</sup>. The yield of the heptyltetralin fraction (IV) amounted to 49.5%; that of the decyltetralin fractions (VIII and IX) to 48.3% and that of the dodecyltetralin fractions (XIII and XIV) to 38.5% calculated on the alcohol used. The yields of alkyltetralins, calculated on the amount of tetralin that reacted, amounted to ~70%. The infrared spectra of the alkyltetralin fractions showed bands at 725, 810, 830, 1610, 1750, 1850, 1885, 2000 cm<sup>-1</sup>. These bands correspond with the spectrum of 1,2,4-trisubstituted benzene [6] and to the spectrum of 6-ethyltetralin [4]. Consequently, the alkyltetralins we prepared had an alkyl group at position 6 in the aromatic ring:

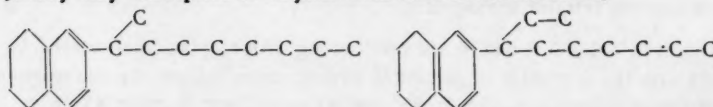


The results of the determination of the number of CH<sub>2</sub> and CH<sub>3</sub> groups, according to the method we described previously [3], are shown in Table 2. From the data in Table 2 it can be seen that heptyltetralin, obtained on alkylating heptene-1 [2] and heptyl alcohol, has identical structure.

TABLE 1. Results of the Alkylation of Tetralin by Alcohols

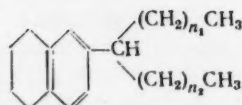
Fraction No.	B.p. °C	Pressure in mm	Yield of fraction, g	n <sub>D</sub> <sup>20</sup>	d <sub>4</sub> <sup>20</sup>	MR for corresp. alkyltetralins	
						calculated	found
Alkylation by n-heptanol-1							
I	90—95	atm	12,1	1,4010	0,7080	—	—
II	200—204	"	27,2	1,5400	0,9695	—	—
III	125—145	4	5,0	1,4815	—	—	—
IV	145—150	4	57,0	1,5180	0,9233	74,91	74,51
Alkylation by n-decyl alcohol							
V	35—45	4,5	16,1	1,4210	0,7405	—	—
VI	69—75	4,5	21,0	1,5420	0,9701	—	—
VII	103—158	4,5	5,2	1,4825	0,8824	—	—
VIII	158—160	4,5	35,5	1,5045	0,9092	88,75	88,43
IX	160—171	4,5	30,0	1,4975	0,8972	88,75	87,50
Alkylation by n-dodecyl alcohol (molar ratio of tetralin to alcohol, 2 : 1)							
X	65—75	4,5	45,0	1,5360	0,9690	—	—
XI	75—80	4,5	10,1	1,4320	0,7640	—	—
XII	100—120	4,5	1,3	1,4440	0,8292	—	—
XIII	184—187	4,5	18,0	1,5060	0,9053	98,00	98,86
XIV	187—197	4,5	14,5	1,5100	0,9111	98,00	98,40
XV	203—215	4,5	6,1	1,4500	Hydrocarbon separated with m.p. 35°		

In order to determine the structure of nonyltetralin, which we had prepared previously [1], the fraction boiling in the broad range 190-200° (9 mm) was subjected to careful distillation in a vacuum at 3 mm. Two basic fractions were obtained: a) b. p. 152-153°; n<sub>D</sub><sup>20</sup> 1,5080; d<sub>4</sub><sup>20</sup> 0,9048 and b) b. p. 153-155°; n<sub>D</sub><sup>20</sup> 1,5130 and d<sub>4</sub><sup>20</sup> 0,9100.\* C<sub>19</sub>H<sub>30</sub>. Calculated MR 84,14, found MR 84,87 and 85,11. These fractions have ten CH<sub>2</sub> groups and two CH<sub>3</sub> groups (see Table 2); consequently they correspond to alkyltetralins with an iso-structure.



\* 6-Methyloctyltetralin and 6-ethylheptyltetralin have n<sub>D</sub><sup>20</sup> 1,5079 and 1,5110, and d<sub>4</sub><sup>20</sup> 0,9077 and 0,9112 respectively [7].

The values found for the molecular refraction of the decyltetralin (Table 1, fr. VIII and IX) and the dodecyltetralin fractions (Table 1, fr. XIII and XIV) correspond well with the calculated values. These fractions are apparently isomeric alkyltetralins. This assumption is confirmed by the data from the infrared spectra (see Table 2). Thus, on alkylating tetralin by primary alcohols and alkenes-1 under the conditions we used, 6-isoalkyltetralins of the following general formula are formed:



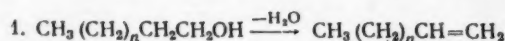
where  $n_1$  may be equal to zero, one or above;  $n_2$  is the number of methylene groups in the longest part of the alkene chain from the double bond;  $n_1 + n_2 = n$  is equal to the number of methylene groups in the original alkene molecule or in the one that is formed.

TABLE 2.

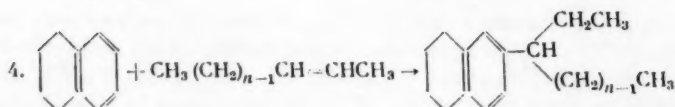
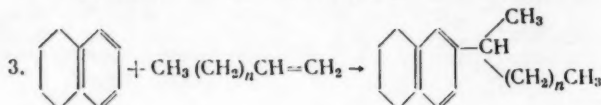
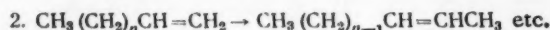
Results of Studies of the Spectra of Alkyltetralins

Fraction No.	Alkyltetralins	$\epsilon_1$	$n_1$	$\epsilon_2$	$n_2$	Remarks
IV	n-Heptyltetralin	625	10	95	1	Calibration
	Heptyltetralin	470	8	214	2	Obtained from alkylation of heptene-1 [2]
	Heptyltetralin	480	8	200	2	
	Nonyltetralin	600	10	207	2	Obtained from alkylation of n-nonyl alcohol
	Nonyltetralin	535	10	202	2	
VIII	Decyltetralin	655	11	210	2	
IX	Decyltetralin	675	11	186	2	
XIII	Dodecyltetralin	875	13	190	2	
XIV	Dodecyltetralin	770	12.0	252	2.5	

The results obtained give reason to assume that the alkylation of tetralin by alcohols proceeds as follows:



Furthermore, a partial isomerization of the alkene-1 that is formed may occur:



Other isomeric alkenes alkylate tetralin analogously.

From the data shown in Table 1 it can be seen that along with alkylation of tetralin by alkenes, a dimerization of the latter occurs with the formation of paraffinic hydrocarbons, apparently due to an oversupply of hydrogen. Thus, a hydrocarbon of composition  $\text{C}_{24}\text{H}_{50}$ , m. p.  $35^\circ$  was separated from fraction XV, b. p.  $203-215^\circ$  (4.5 mm). In



the remaining fractions the presence of dimers may be assumed on the basis of the somewhat lower values of the index of refraction of the corresponding fractions. Thus, in fraction III a hydrocarbon of  $C_{14}$  composition may be present and in fraction IX, one of  $C_{20}$  composition.

The combination dispersion spectra were taken by G. K. Galvoronskaya, to whom the authors express their thanks.

#### SUMMARY

1. The possibility of alkylating tetralin by primary alcohols of normal structure and containing  $C_7$ ,  $C_{10}$  and  $C_{12}$  in the liquid phase with the formation of 6-alkyltetralins of branched structure was demonstrated.
2. The yields of isoheptyl-, isodecyl- and isododecyltetralins amount to 49.5, 48.3 and 38.5% respectively, based on the original alcohol, and to ~70% of theoretical based on the tetralin that reacts.

#### LITERATURE CITED

1. N. I. Shuikin and N. A. Pozdnyak, *Izv. AN SSSR, Otd. Khim. Nauk* 1960, 1094.
2. N. I. Shuikin, N. A. Pozdnyak, and V. A. Shlyapochnikov, *Izv. AN SSSR, Otd. Khim. Nauk* 1960, 125.
3. N. I. Shuikin, V. A. Shlyapochnikov, N. A. Pozdnyak, and B. L. Lebedev, *Izv. AN SSSR, Otd. Khim. Nauk* 1961, 466.
4. C. M. Staveley and J. C. Smith, *J. Inst. Petrol.* 42, 55 (1956).
5. Yu. P. Egorov, V. A. Shapochnikov, and A. D. Petrov, *Zh. prikl. khimii* 14, 617 (1959).
6. C. W. Yong, R. R. Duvall, and N. Wright, *Analyt. Chem.* 23, 709 (1951).
7. N. I. Shuikin, B. L. Lebedev, and N. A. Pozdnyak, *Doklady Akad. Nauk SSSR* 131, 335 (1960).

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. Some or all of this periodical literature may well be available in English translation. A complete list of the cover-to-cover English translations appears at the back of this issue.

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# THE PREPARATION OF PYRYLIUM SALTS

## BY THE BISACYLATION OF OLEFINS

### COMMUNICATION 5. THE BISACETYLATION OF DI- AND TRIISOBUTYLENE

A. T. Balaban, A. Genya, and C. D. Nenitzescu

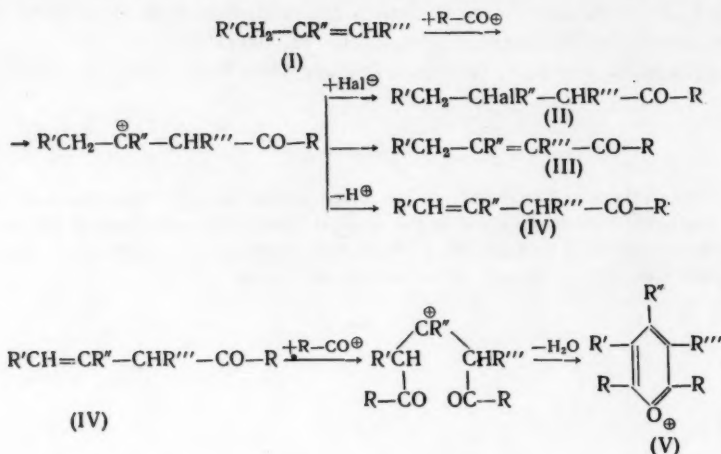
Polytechnic Institute, Bucharest

Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*,

No. 6, pp. 1102-1107, June, 1961

Original article submitted January 30, 1961

The preparation of pyrylium salts by the acylation of olefins [1-5] according to the Friedel-Crafts reaction is based on the fact that on the monoacylation of an olefin (I) derived from propylene, a  $\beta, \gamma$ -unsaturated ketone (IV) exists in the reaction mixture in equilibrium with a  $\beta$ -haloketone (II) and with an  $\alpha, \beta$ -unsaturated ketone (III). As long as the double bond of (IV) is not linked with a carbonyl group, it may interact with a new acyl-cation and then, through the splitting off of water, a pyrylium cation (V) is formed in accordance with the following reactions:

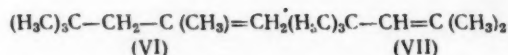


Unlike acylation products (II), (III) and (IV), the pyrylium salts (V), as a rule, are soluble in water and therefore for a long time remained unnoticed; they may be separated either by precipitation from the aqueous solution as chlorates, or by indirect conversion to pyridines by means of the reaction with ammonia which proceeds easily.

The acetylation of diisobutylene has been studied by a number of authors [6-10]; among them Byrns and Doumani [6-8] noticed that on acetylation by means of acetic anhydride in the presence of zinc chloride, a crystalline product is formed which may be separated from the reaction mixture by filtration, and to which the structure of "a complex of 1,3-diketone with zinc chloride" was ascribed. The paper does not give any analytical data, but states that the "complex" cannot be decomposed into its components, and that as a result of reaction with ammonia the "complex" is converted into a nitrogen-containing base.

These observations lead to the thought that this "complex" is actually a pyrylium salt; therefore the present study was undertaken in which the monoacetylation products were not separated, but only the polyacetylation products.

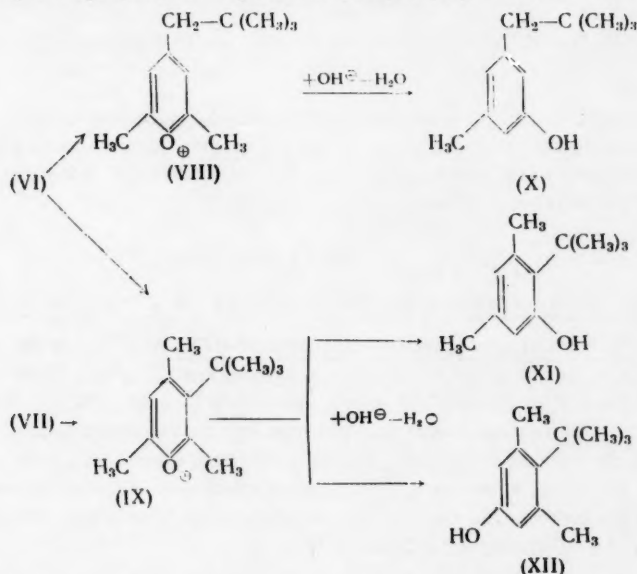
Diisobutylene is a mixture of two isomers: 2,2,4-trimethylpentene-4 (VI) 80% and 2,2,4-trimethylpentene-3 (VII) 20% [11, 12]:



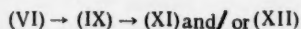
Previous studies of acetylation were carried out on mixtures [6, 8, 10]. An exception is the paper [9] in which both components, separated from each other by distillation through a column with 200 theoretical plates, were each acetylated individually. An unexpected result was the fact that identically the same reaction products were obtained from both isomers: a  $\beta, \gamma$ -unsaturated ketone and two cis-trans stereoisomeric forms of an  $\alpha, \beta$ -unsaturated ketone in quantities that varied with the catalyst — which included  $\text{H}_2\text{SO}_4$ , acetylsulfoacetic acid,  $\text{ZnCl}_2$ ,  $\text{SnCl}_2$  and  $\text{BF}_3$ . Analysis of the unreacted olefin show that it consisted of an equilibrium mixture of 80% (VI) + 20% (VII). From this it follows that in the Friedel-Crafts reaction, under the influence of catalysts, the achievement of a state of equilibrium of both isomers of diisobutylene takes place more rapidly than their acetylation. For this reason an equilibrium mixture was used in the present study.

Acetylation in the presence of  $\text{ZnCl}_2$  under the conditions described above [6] does indeed lead to the formation of a product which precipitates from the reaction mixture in crystalline form, and from which it may be separated by filtration, washing with ether and recrystallization from acetic acid; it is easily soluble in water, while analysis of the elements shows that it corresponds to the formula  $\text{C}_{12}\text{H}_{19}\text{O}^\ominus \text{ZnCl}_3^\ominus$ . If it is dissolved in water and treated with perchloric acid, a chlorate precipitates out which may be recrystallized from water; it corresponds to the formula  $\text{C}_{12}\text{H}_{19}\text{O}^\ominus \text{ClO}_4^\ominus$ . On treatment of the zinc salt or chlorate with ammonia, the base  $\text{C}_{12}\text{H}_{19}\text{N}$  is formed which was converted into the picrate, picrolonate and chloroplatinate corresponding to this formula. Heating the chlorate with a solution of caustic alkali yields a phenol,  $\text{C}_{12}\text{H}_{18}\text{O}$ , which was converted into a phenylcarbamate and a dibrom derivative. These facts are easy to explain if we assume the formation of the pyrylium salt  $\text{C}_{12}\text{H}_{19}\text{O}^\oplus \text{X}^\ominus$ . The conversion of pyrylium salts into pyridines or phenols is well known [1, 5, 13].

Study of the monoacetylation of diisobutylene showed [9, 10] that the monoacetyl derivatives are derivatives of isomer (VI), which is predominant in the reaction mixture and possess a more reactive terminal double bond. The structure of the pyrylium salt may be expressed either by formula (VIII) or (IX).



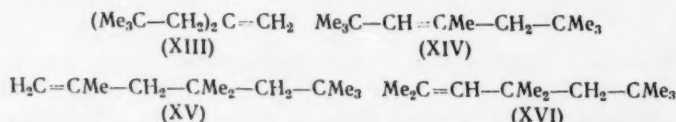
A choice between these two formulas may be made on the basis of the conversion of this compound into phenol: phenol (X), which should be obtained from (VIII), may give a tribrom derivative; while phenols (XI) or (XII), which must be obtainable from (IX) may only give dibrom derivatives. As a matter of fact the original phenol gives a dibrom derivative, so that it follows from the above scheme that these reactions do indeed occur:



In order to find out whether or not more energetic catalysts would lead to the formation of more symmetrical structures (in our case VIII), as was observed in the case of 2-methylbutene-2 [2], the acetylation of diisobutylene by acetyl chloride in the presence of aluminum chloride was also studied. This catalyst had not yet been used in studies of the acetylation of diisobutylene. The product obtained was found to be identical with (IX) (comparison of derivatives of the corresponding pyridines were made). However, unlike the reaction carried out in the presence

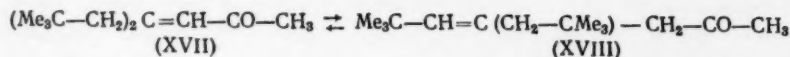
of zinc chloride, this reaction still gave two other pyran compounds from isobutylene: 2,4,6-trimethylpyrylium chlorate as a result of the bisacetylation of isobutylene, and a pyrone derivative  $C_{10}H_{12}O_2$  with a m. p. of 92°. These compounds, which are easily prepared by the trisacetylation of isobutylene in the presence of aluminum chloride, will be described separately.

The literature also contains studies on the acetylation of triisobutylene [14, 15]. Triisobutylene is a mixture of four isomers: (XIII) 54%; (XIV) 36%; (XV) + (XVI) 10% [11, 12, 16, 17]:



The most resistant of these to oxidation by permanganate is (XIII) and in this way it may be separated from the other isomers. Acetylation of the mixture (XIII) - (XVI) [14, 15] and the isomer (XIII) [15] (according to Kondakov) by means of acetic anhydride in the presence of zinc chloride, was studied, and the unsaturated ketone (XVII) was identified.

Study of the bisacetylation of triisobutylene by acetic anhydride in the presence of zinc chloride showed that the same pyrylium salt is formed with an anion of  $ZnCl_3^-$  as is formed from diisobutylene. Acetylation by means of acetyl chloride in the presence of aluminum chloride gave the same pyran reaction products as did diisobutylene. The fact that the bisacetylation of triisobutylene as such does not yield the pyrylium salt is not something unexpected since the introduction of a second acetyl group into the unsaturated ketone (XVII) [speaking more accurately, the  $\beta, \gamma$ -unsaturated ketone (XVIII)] meets considerable spatial difficulties.



It should be noted that in the presence of  $ZnCl_2$ , diisobutylene forms a pyrylium salt which does not undergo depolymerization, while triisobutylene gives the same pyrylium salt with partial depolymerization. In the presence of  $AlCl_3$ , di- and triisobutylene, as a result of deep depolymerization to isobutylene, give identically the same pyran compounds which are derivatives of mono- and diisobutylene.

## EXPERIMENTAL

### Acetylation of Diisobutylene in the Presence of Zinc Chloride

2,4,6-Trimethyl-3-tert.butylpyrylium chlorozincate (IX). At 0° and in the absence of moisture, 102 g (1 M) of acetic anhydride is added to 110 g (0.8 M) of anhydrous zinc chloride. Then, with cooling and stirring, 56 g (0.5 M) of diisobutylene b. p. 100-105° is slowly added drop by drop. The mixture is stirred at room temperature for four hours and allowed to stand overnight. The next day the reaction mixture contains crystals. One hundred ml of ether is added, the solution filtered off, and the precipitate washed with ether. Thirty-two g of a colorless product, easily soluble in water, is obtained. The aqueous solution is yellowish because of partial hydrolysis; the solution is colorless in 5% hydrochloric acid. After recrystallization from acetic acid the m. p. is 219°. Found: C 41.48; H 5.60%.  $C_{12}H_{19}O^+ZnCl_3^-$ . Calculated: C 41.06; H 5.46%.

The chlorate is prepared by treatment with a cold solution of chlorozincate in a 5% hydrochloric acid solution of perchloric acid. An oil separates which crystallizes when touched with a glass rod; after recrystallization from water the m. p. is 105°. Found: C 51.53; H 6.73%.  $C_{12}H_{19}O^+ClO_4^-$ . Calculated: C 51.71; H 6.87%.

2,4,6-Trimethyl-3-tert. butylpyridine is prepared by the treatment of the chlorozincate or chlorate by aqueous ammonia; the mixture is extracted with ether, the solution dried over caustic soda, and distilled in vacuo, b. p. 136° (60 mm),  $n_D^{25}$  1.4909;  $d_4^{25}$  0.8957; MR 57.23 found, MR 57.18 (calculated from bond increments), MR 57.96 (calculated from atomic increments).

Picrate, m. p. 146-147° (from ethyl alcohol). Found: C 53.01, N 5.51, N 13.61%.  $C_{18}H_{22}N_4O_7$ . Calculated: C 53.20, H 5.45, N 13.79%.

Picrolonate, m. p. 208° (from ethyl alcohol). Found: N 15.78%.  $C_{22}H_{27}N_5O_5$ . Calculated: N 15.87%.



Chloroplatinate, m. p. (with decomposition) 241° (from 10% hydrochloric acid). Found: C 37.96, H 5.53, N 4.10%.  $C_{12}H_{19}N \cdot \frac{1}{2}H_2PtCl_6$ . Calculated: C 37.70, H 5.27, N 3.66%.

The conversion of pyrylium chlorate (IX) to phenol takes place with a 36% yield by the addition of the chlorate to a boiling aqueous solution of caustic soda (four equivalents). Phenol is only slightly soluble in caustic soda. After cooling, the solution is extracted with ether which is then distilled off, and the remainder is left in the cold until crystallization occurs. On recrystallization from ether, the product melts at 42°. Found: C 80.65, H 10.13%.  $C_{12}H_{18}O$ . Calculated: C 80.85, H 10.18%.

Phenylurethan, m. p. 82° (from 50% ethyl alcohol). Found: C 77.10, H 7.95, N 5.48%.  $C_{19}H_{23}NO_2$ . Calculated: C 76.76, H 7.74, N 4.91%.

On bromination in chloroform or in carbon tetrachloride, the phenol takes up two moles of bromine and a liquid dibrom derivative is formed. Consequently the phenol corresponds to (XI) or (XII) or to a mixture of both.

#### The Acetylation of Triisobutylene in the Presence of Zinc Chloride

This was carried out as in the case of diisobutylene. Seventeen g of triisobutylene (b. p. 70-180°), four equivalents of acetic anhydride and two equivalents of zinc chloride are used. The next day the clear green solution is poured into ice water and hydrochloric acid, the unsaturated Ketone is extracted with ether, and the aqueous solution is allowed to stand in the cold. After two days crystals of the chlorozincate appear, which, after recrystallization from a mixture of ethyl alcohol and ether or acetic acid, melt at 218°. A mixed melting point with the chlorozincate obtained from diisobutylene showed no depression. Analysis: C 41.58, H 5.32%.

#### The Acetylation of Diisobutylene in the Presence of Aluminum Chloride

Eighty g (0.6 M) of anhydrous aluminum chloride, with stirring and cooling, is added to 117 g (1.5 M) of acetyl chloride; then, also with stirring and cooling, 33 g (0.3 M) of diisobutylene is slowly added drop by drop. Stirring is continued for two hours at room temperature, and the mixture allowed to stand overnight. Then it is hydrolyzed with 350 g of ice and 30 ml of concentrated hydrochloric acid; the mixture is extracted with ether and the aqueous solution is treated with 60 ml of 60% perchloric acid. Oily drops separate out which partially crystallize on standing at 0° for one or two hours. The product is filtered off and 4 g of 2,4,6-trimethylpyrylium chlorate are obtained and washed with a small quantity of water; m. p. 245° (from water). The identity of this product was determined by the absence of depression in a mixed melting point test with the known product, and also by conversion to symmetrical collidine, the picrate of which melts at 158° and shows no depression in a mixed melting point test with a known sample [1].

Ether is added to the filtrate and an upper layer of the oily chlorate forms which is treated in the cold with aqueous ammonia. The aluminum hydroxide is filtered off and carefully washed with ether; then the ether layer is dried over caustic soda and distilled in vacuo. A 6.5 g fraction boiling at 130-160° at 60 mm and corresponding to 2,4,6-trimethyl-3-tert. butylpyridine is obtained; mixed m. p. tests of the picrates and chloroplatinates show no depression. The material remaining in the flask crystallizes on cooling (2.5 g). The product may be purified by steam distillation and distillation in vacuo, or by recrystallization from petroleum ether, or from 60% alcohol; m. p. 92°; it is a pyrone compound  $C_{10}H_{12}O_2$  which may be converted into: the picrate, m. p. 134°; picrolonate, m. p. 155°; chloroplatinate, m. p. 182° (with decomposition); bromohydrate, m. p. 205°; chloroferrate, m. p. 138°; with ammonia in a sealed tube it may be converted to pyridone  $C_{10}H_{13}NO$  (chloroplatinate, m. p. 202°; picrate, m. p. 101-102°; picrolonate, m. p. 222°). On boiling with an aqueous solution of caustic soda, 30% of sym. m-xylene and 60% of the ketophenol  $C_{10}H_{12}O_2$ , b. p. 207° at 40 mm are formed (2,4-dinitrophenylhydrazones, m. p. 160°; phenylcarbamate, m. p. 70°), which gives  $C_{10}H_{11}Br_4O_2$ , m. p. 136°, on treatment with bromine. The reaction of pyrone with hypobromite gives the bromopyrone  $C_{10}H_{11}BrO_2$ , m. p. 103° (picrolonate, m. p. 122°).

This pyrone compound, which is also obtained in satisfactory yield from acetyl chloride, tert. butyl chloride and aluminum chloride, will be described in a subsequent paper. On the basis of the data given, and also from the ultraviolet and infrared spectra and the nuclear magnetic resonance spectra, it appears probable that this compound has the structure of a vinylone of dimethylpyrone.

#### The Acetylation of Triisobutylene in the Presence of Aluminum Chloride

This is carried out as in the case of diisobutylene. Eighty ml of acetyl chloride, 50 g of aluminum chloride and 37 g of triisobutylene were used. This was worked up in similar fashion, and yielded 3 g of 2,4,6-trimethylpyrylium chlorate, 5 g of 2,4,6-trimethyl-3-tert. butylpyridine (the identity of which was established by mixed melting points of the picrates and chloroplatinates) and 2 g of a pyrone compound  $C_{10}H_{12}O_2$ .

## SUMMARY

1. The "complex with  $ZnCl_2$ ", previously obtained on the acetylation of diisobutylene, is actually a pyrylium salt.

2. This pyrylium salt was converted into the corresponding pyridine and phenol. From the data obtained on brominating this phenol, it follows that the structure of the pyrylium salt corresponds to (IX), i.e., that it is 2,4,6-trimethyl-3-tertbutylpyrylium.

3. Acetylation of diisobutylene in the presence of  $AlCl_3$  yields, along with (IX), trimethylpyrylium formed by the bisacetylation of isobutylene, the pyrone compound  $C_{10}H_{12}O_2$  formed by the trisacetylation of the same monomeric olefin.

4. The acetylation of triisobutylene in the presence of  $ZnCl_2$  also gives the pyrylium salt (IX), while in the presence of  $AlCl_3$  the same three products are formed as in the case of diisobutylene and  $AlCl_3$ .

## LITERATURE CITED

1. A. T. Balaban and C. D. Nenitzescu, *Liebig's Ann. Chem.* **625**, 74 (1959).
2. A. T. Balaban and C. D. Nenitzescu, *J. Chem. Soc.* (in press).
3. A. T. Balaban and C. D. Nenitzescu, *J. Chem. Soc.* (in press).
4. A. T. Balaban, M. Gavat, G. Mateescu, and C. D. Nenitzescu, *J. Chem. Soc.* (in press).
5. A. T. Balaban and C. D. Nenitzescu, *Studii si Cercetari Chim.* **9**, 251 (1961).
6. A. C. Byrns and T. F. Doumani, *Industr. and Engng. Chem.* **35**, 349 (1943).
7. U. S. Pat. 2315046; *Chem. Abstrs.* **37**, 5416 (1943); U. S. Pat. 2355703; *Chem. Abstrs.* **39**, 87 (1945); U. S. Pat. 2411823; *Chem. Abstrs.* **41**, 1234 (1947); U. S. Pat. 2438334; *Chem. Abstrs.* **42**, 4602 (1948); U. S. Pat. 2463742; *Chem. Abstrs.* **43**, 4685 (1949).
8. U. S. Pat. 2453619; *Chem. Abstrs.* **43**, 2634 (1949).
9. P. Arnaud, *Compt. rend.* **244**, 1785 (1957).
10. A. P. Meshcheryakov, L. V. Petrova, and Yu. P. Egorov, *Zh. obshch. khimii* **28**, 2588 (1958); A. P. Meshcheryakov, L. V. Petrova, and A. D. Petrov, *Izv. AN SSSR, Otd. Khim. Nauk* **1960**, 98.
11. F. C. Whitmore and co-author, *J. Amer. Chem. Soc.* **63**, 2035 (1941); *Industr. and Engng. Chem.* **26**, 94 (1934).
12. Ya. T. Eldus and B. K. Nefedov, *Uspekhi khimii* **29**, 883 (1960).
13. K. Dimroth, *Angew. Chem.* **72**, 331 (1960).
14. A. M. Petrov and E. P. Kaplan, *Izv. AN SSSR, Otd. Khim. Nauk* **1947**, 302.
15. A. P. Meshcheryakov and L. V. Petrova, *Izv. AN SSSR, Otd. Khim. Nauk* **1951**, 576.
16. A. P. Meshcheryakov, M. I. Batuev, and A. D. Petrov, *Izv. AN SSSR, Otd. Khim. Nauk* **1950**, 282; M. I. Batuev, A. P. Meshcheryakov, and A. D. Matveeva, *Izv. AN SSSR, Otd. Khim. Nauk* **1958**, 75; A. P. Meshcheryakov and E. N. Erzyutova, *Doklady Akad. Nauk SSSR* **124**, 826 (1959).
17. P. D. Bartlett, *J. Amer. Chem. Soc.* **67**, 141 (1945); **77**, 2861 (1955).

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. Some or all of this periodical literature may well be available in English translation. A complete list of the cover-to-cover English translations appears at the back of this issue.

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# TAUTOMERISM OF NITRO COMPOUNDS

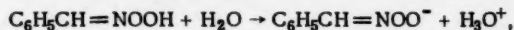
## COMMUNICATION 3. THE INFLUENCE OF TEMPERATURE AND ION STRENGTH OF SOLUTIONS ON THE RATE OF TAUTOMERIC CONVERSION OF PHENYLNITROMETHANE

V. M. Belikov, S. G. Mairanovskii, Ts. B. Korchemnaya  
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Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*,  
No. 6, pp. 1108-1111, June, 1961  
Original article submitted June 22, 1960

We have shown previously that in a strong acid solution the rate of isomerization of the aci form of phenylnitromethane to the nitro form is determined by the degree of dissociation of the nitro form [1]. The dissociation rate of the aci form was comparatively small:  $k = 4.14 \cdot 10^{-5}$  liters  $\cdot$  M $^{-1} \cdot$  sec $^{-1}$ . This rate is much lower than the dissociation rate of other oxygen acids (see, for example [2, 3]). The only way in which aciphenylnitromethane differs from other acids, is the presence of a double bond at the atom that carries the hydroxyl group. This fact, apparently, is expressed in the rate of dissociation and recombination, since the dissociation constant of this acid has a normal value:  $pK_A = 3.9$ . In order to make a complete investigation of this process, we studied the dependence of the rate of isomerization of aciphenylnitromethane to phenylnitromethane at various temperatures, both at low values of pH, where the isomerization rate is determined by the dissociation of the aci form by the action of water, and in the pH 4.7-6 region, where the isomerization rate is determined by the recombination of an anion with the formation of the nitro form of phenylnitromethane. All experiments were carried out at a constant ion strength of the solutions:  $\mu = 0.2$ . Constancy of the ion strength was obtained by the addition of KCl.

The measurements and the processing of the results were carried out in accordance with methods described previously [1]. Figure 1 shows the dependence of the logarithm of the first order rate constant on the pH of the solution. As can be seen from Fig. 1, at a given temperature, the curves show that the relationship is practically constant. Figure 2 shows the dependence of  $\log k_{AD}^{H_2O}$  on  $1/T$ , which makes it possible to calculate the activation energy of the dissociation of aciphenylnitromethane by the action of water as a base:



$E_{akt}$  of this process has a value of 17,400 cal/M. The Arrhenius equation for this reaction has the form

$$k_{AD}^{H_2O} = 2.5 \cdot 10^8 \cdot e^{-\frac{17400}{RT}}$$

The magnitude of the preexponential factor is considerably less than the theoretical which indicates that the steric factor is of great importance in this reaction. This apparently explains the low dissociation rate of aciphenylnitromethane. Examination of a hemispheric model of aciphenylnitromethane shows the absence of free rotation between a carbon atom of the benzene ring and an atom of carbon carrying a nitro group. Moreover, the coplanarity of the benzene ring and the C=N bond cannot be achieved without a considerable change in the angles which may also be expressed in the steric factor of the reaction.

We studied the recombination of an anion with the formation of the undissociated nitro form of phenylnitromethane in acetate buffered solutions. The individual rates  $k_{NR}^{H_3O^+}$  and  $k_{NR}^{CH_3COOH}$  were determined by special experiments only at 25° (1). At the remaining temperatures, the observed rate of recombination was the sum of the two rates:

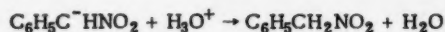
$$k = k_{NR}^{H_3O^+} [H_3O^+] + k_{NR}^{CH_3COOH} [CH_3COOH]$$

In order to determine individual partial rates, we modified the equation as follows:

$$\frac{k}{[H_3O^+]} = k_{NR}^{H_3O^+} + k_{NR}^{CH_3COOH} \frac{[CH_3COOH]}{[H_3O^+]}$$

Having plotted the dependence of  $k/[H_3O^+]$  on  $[CH_3COOH]/[H_3O^+]$ , we determined the partial constants for the remaining temperatures. Because of the wide scattering of the points, however, it was impossible to determine the values of these constants with sufficient precision; therefore in Fig. 3 and 4 in constructing the curves for finding the activation energy, the limits of the errors in calculating these constants were plotted. In the figures the average arithmetic values are indicated by small circles. The activation energies obtained from these curves are not very precise; however they make it possible to evaluate the preexponential factor, which is close to the theoretical.

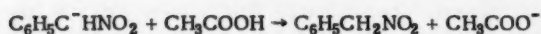
The Arrhenius equation for the process



has the form

$$k_{NR}^{H_3O^+} = 10^{11} e^{-\frac{12000}{RT}},$$

and for the process



it has the form

$$k_{NR}^{CH_3COOH} = 10^{13.7} e^{-\frac{19500}{RT}}$$

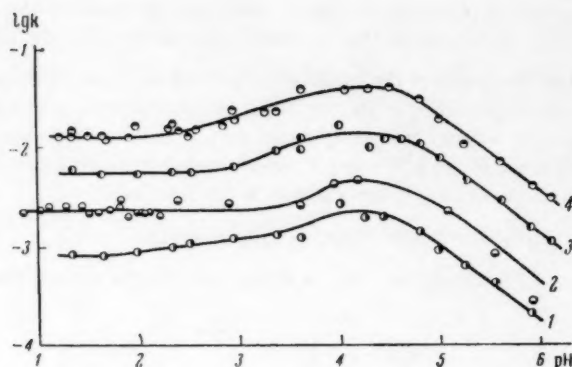


Fig. 1. Dependence of the logarithm of the constant of the rate of isomerization of the aci form of phenylnitromethane to the nitro form ( $\text{sec}^{-1}$ ) on pH. 1) 15°; 2) 25°; 3) 35°; 4) 45°.

For a trustworthy calculation of the partial rate constants of the reactions [1] it is also necessary to examine the influence of ion strength on the rate of these processes. A special study showed that increasing the ion strength of the solutions to  $\mu = 1$  (and even to 3.7 for the dissociation of the aci form) has very little effect on the rate of the reactions. The influence of ion strength on the rate constant of the reaction is described by the equation [4]

$$\lg k = \lg k_0 + \alpha \sqrt{\mu} \quad (1)$$

where  $\alpha$ , for aqueous solutions, has the value  $1.02 Z_A Z_B$ ;  $Z_A$  and  $Z_B$  are the charges on the reacting particles. We found that for the dissociation of aciphenylnitromethane at pH 1,  $\alpha = -0.04$ , and at pH 2.2,  $\alpha = +0.1$ . Small values of  $\alpha$  for this process are explained by the fact that one of the reacting particles is an unchanged molecule, i.e.,  $Z_A$  (or  $Z_B$ ) is equal to 0, in consequence of which  $\alpha$  is also close to 0 and  $\log k = \log k_0 = \text{constant}$ . For the recombination



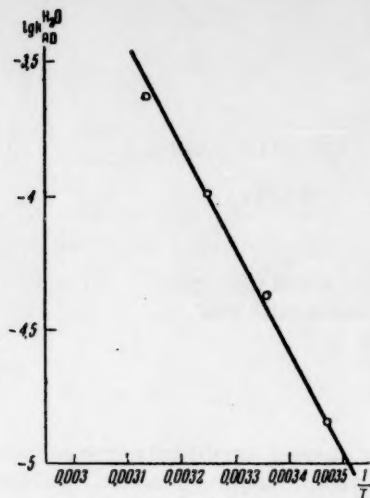


Fig. 2. Dependence of the logarithm of the rate constant of dissociation of the aci form ( $\text{liters} \cdot \text{M} \cdot \text{sec}^{-1}$ ) on the reciprocal of the temperature.

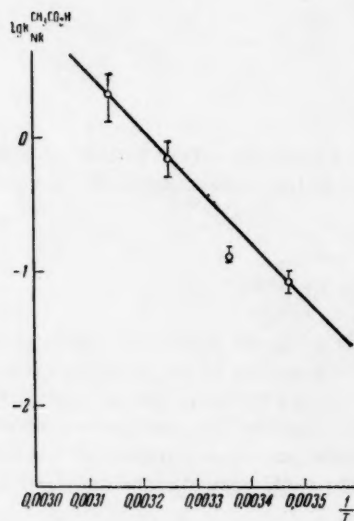


Fig. 4. Dependence of the logarithm of the rate constant of recombination of the nitro form by the action of  $\text{CH}_3\text{COOH}$  ( $\text{liters} \cdot \text{M} \cdot \text{sec}^{-1}$ ) on the reciprocal of the temperature.

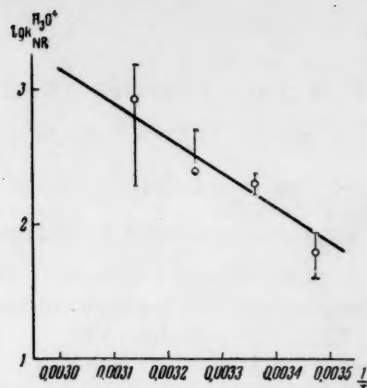


Fig. 3. Dependence of the logarithm of the rate constant of recombination of the nitro form by the action of  $\text{H}_3\text{O}^+$  ( $\text{liters} \cdot \text{M} \cdot \text{sec}^{-1}$ ) on the reciprocal of the temperature.

reaction of phenylnitromethane at pH 5 in a buffer solution consisting of  $\text{NaH}_2\text{PO}_4 + \text{KCl} + \text{HCl}$ ,  $\alpha = +0.3$ . In this case both reacting particles have a negative charge  $\text{C}_6\text{H}_5\text{C}^-\text{HNO}_2 + \text{H}_2\text{PO}_4^- \rightarrow \text{C}_6\text{H}_5\text{CH}_2\text{NO}_2 + \text{HPO}_4^{2-}$  and therefore  $\alpha > 0$ . In accordance with Eq. (1),  $\alpha$  must have a value of +1; however it should be born in mind that this equation is valid for very small ion strengths and with increasing salt concentration the influence of the ion strength decreases [4].

#### SUMMARY

1. The comparatively small dissociation rate of aciphenylnitromethane is explained by a significant steric factor. The recombination of phenylnitromethane proceeds normally.
2. The ion strength of the solutions has very little influence on the rate of the processes studied.

#### LITERATURE CITED

1. S. G. Maïranovskii, V. M. Belikov, Ts. B. Korchemnaya, V. A. Klimova, and S. S. Novikov, *Izv. AN SSSR, Otd. Khim. Nauk* 1960, 1787.
2. R. P. Bell, *Quart. Revs.* 13, N 3, 169 (1959).
3. G. G. Hammes and L. E. Erickson, *J. Chem. Educ.* 35, 612 (1958).
4. A. I. Shatenshtein, *Theory of Acids and Bases*, Goskhimizdat, M. - L. (1949), p. 196 [in Russian].

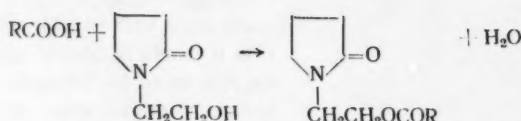
## STUDIES OF THE LACTONES AND LACTAMS

## COMMUNICATION 20. THE REACTION OF N-(CHLOROALKYL) LACTAMS WITH ALCOHOLS

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Original article submitted May 27, 1960

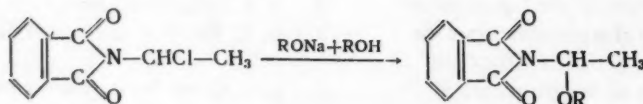
The introduction of a lactam ring into the structure of organic compounds significantly increases their value in a number of cases. The ability to form complexes, affinity for dyestuffs, hydrophilic character, solubility, etc., are all improved. These properties are of great interest not only for commercial products, but also for pharmaceutical materials [1-5]. Previously a reaction was proposed that would make it possible to use the carboxyl group of these compounds for the introduction of a lactam ring into their structure. The active reagent was N-( $\beta$ -hydroxyethyl)-pyrrolidone. Esters containing the pyrrolidone ring were prepared by the esterification of this alcohol by monobasic fatty acids or by their chlorides. An interesting property of these esters is their ability to dissolve not only in organic solvents, but also in water [6].



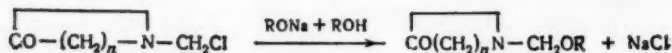
In the present study a method of introducing the lactam ring into the structure of compounds containing a hydroxyl group was worked out. The reaction of alcohols or of alcoholic solutions of alcoholates with N-( $\alpha$ -chloroalkyl)- and N-( $\beta$ -chloroalkyl)lactams was studied for this purpose.



At the same time the problem arose of explaining the activity of the halogen atom in N-(chloroalkyl)lactams depending on its position relative to the lactam ring, and to compare the properties of the halogen atom in these compounds with the properties of halogen in some oxygen-containing analogs ( $\alpha$ -chloro- and  $\beta$ -chloroalkyl esters). As a representative of the N-( $\alpha$ -chloroalkyl)lactams we used N-(chloromethyl)lactams which were synthesized and described previously [4, 5]. The reaction of N-(chloromethyl)lactams with alcohols and alcoholates has not been described in the literature. A similar reaction that is known is that of N-( $\alpha$ -chloroethyl)phthalimide, which has a structure closely similar to the one under study [7].

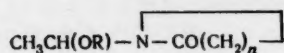


The high activity of the halogen atom in N-(chloromethyl)lactams, observed in the case of the reaction with water and causing these compounds to approach  $\alpha$ -chloroalkyl esters [8], gave foundation for supposing that the reaction of N-chloroalkyl lactams with alcohols and alcoholates would proceed extremely energetically. As a matter of fact, on simply mixing N-(chloromethyl)pyrrolidone and N-(chloromethyl)caprolactam with an alcohol solution of alcoholate, the exchange of an atom of chlorine for an alkoxy radical, is accompanied by strong evolution of heat.

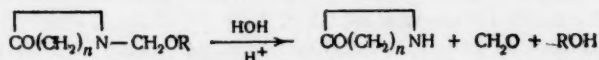


In order to complete the process, the reaction mixture is heated for 0.5-1 hr at a temperature of 40-60°. Study of the influence of the ratio of the components on the yield of the reaction products showed that a fourfold excess of alcohol in relation to chloromethylactam is entirely satisfactory. The use of a smaller quantity of alcohol makes it difficult to prepare the alcoholate. This reaction makes it possible to synthesize the previously unknown N-(alkoxymethyl)lactam series in 60% yield. In the case of N-(chloromethyl)pyrrolidone and butyl alcohol it was shown that the exchange of a halogen atom by an alkoxy group takes place in these compounds even in the absence of alcoholates, i.e., by reaction with pure alcohols. In this case, however, the yield of reaction products is somewhat reduced.

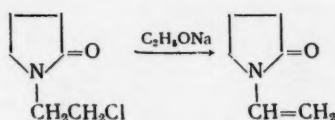
The N-(alkoxymethyl)lactams produced are colorless liquids. Like esters that contain a lactam ring as a substituent [6], these esters are easily soluble not only in organic solvents, but also in water. According to their chemical properties they appear to be nitrogenous analogs of formal, and similar to the alkoxyethylidenelactams in structure



They easily split into lactams, alcohol and aldehyde on treatment with dilute acids [9]

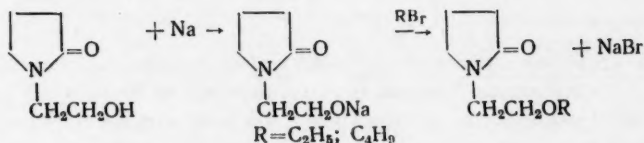


Thus, a halogen atom or an alkoxy group, located in an  $\alpha$ -position to the lactam ring, has a high degree of mobility. It was also of interest to investigate the influence of the lactam ring on the properties of an atom of halogen located in the  $\beta$ -position. As an example of this, the reaction of N-( $\beta$ -chloroethyl)pyrrolidone with an alcohol solution of alcoholate was studied. The reaction of N-( $\beta$ -chloroethyl)pyrrolidone with sodium alcoholate has been described in the literature. But it still remained unclear whether the authors used an alcoholic solution of alcoholate [10] or an alcohol-free alcoholate. In this case the detachment of hydrogen chloride with the formation of vinylpyrrolidone was observed [10].



We repeated this reaction under the conditions we had used for  $\alpha$ -(chloromethyl)lactams, i.e., with an alcoholate in the presence of a fourfold excess of alcohol (methyl or butyl). Under these conditions at a temperature of 30-35° it appeared that the reaction product was vinylpyrrolidone.

Consequently, in the reaction of N-( $\beta$ -chloroethyl)pyrrolidone with alcoholic solutions of alcoholate, detachment of hydrogen chloride occurs, and not the substitution of a halogen atom by an alkoxy group. In this respect N-( $\beta$ -chloroethyl)pyrrolidone occurs only with great difficulty. The N-( $\beta$ -alkoxyethyl)pyrrolidones which were of interest to us were synthesized by the reaction of the alcoholate of N-( $\beta$ -hydroxyethyl)pyrrolidone with halogen alkyls



Thus our study showed the peculiar influence of the lactam ring on the properties of atoms and groups joined to it — the reactivity of halogen atoms and alkoxy groups located in the  $\alpha$ -position to the lactam ring is increased. This influence of the lactam ring is analogous to the action both of ether and of carboxyl and carbonyl groups. In case a halogen atom is located in the  $\beta$ -position to the lactam ring, its ability to exchange becomes more difficult, and the tendency toward detachment as HCl is facilitated. In this case the character of the influence of the lactam ring differs from the influence of an ether group, and corresponds with the action of carboxyl or carbonyl groups.

#### EXPERIMENTAL

Methylolactams and N-(chloromethyl)lactams were prepared according to the method described in [5]. The present paper specifies more precisely the method of purifying methylolactams since the method previously proposed

which involves the reprecipitation of the methylol derivative from benzene solution by means of ether, is extremely laborious because of the low solubility of methylolactams in benzene. In the majority of cases it was found that it was sufficient to wash the methylolactams three times with dioxane and then three times with diethyl ether, followed by drying in vacuum desiccator over calcium chloride. In cases where purification appears inadequate and the product remains moist, it may be subjected to further purification by one of the following methods: 1) washing with a hot solution of acetone, with subsequent precipitation by means of petroleum ether; 2) boiling the N-methylolactams with petroleum ether in an apparatus with a Dean and Stark fitting, as a result of which moisture is removed from the raw product. On cooling the solution, the substance crystallizes out.

The reaction of N-(chloromethyl)- $\alpha$ -pyrrolidone with sodium methylate. 6.67 g of N-(chloromethyl)- $\alpha$ -pyrrolidone was added drop by drop to an alcoholic solution of sodium methylate prepared from 14.6 g of methyl alcohol and 1.15 g of metallic sodium. Immediately a white precipitate came down and the temperature rose from 21 to 57°. On completion of the addition of the chloride, stirring was continued for 20-25 minutes. The precipitate was filtered off (weight 2.65 g) and washed with dry diethyl ether. The extracts obtained were combined with the original filtrate. After distilling off the solvents, a yellowish viscous liquid remained in the flask which, on fractionation yielded N-(methoxymethyl)- $\alpha$ -pyrrolidone (I), b. p. 74-77° (3 mm), weight 3.25 g, yield 64.5%. No less than four fractionations were essential for complete purification of the product. The syntheses of N-(ethoxymethyl)-pyrrolidone (II), N-(butoxymethyl)pyrrolidone (III) and N-(butoxymethyl)caprolactam (IV) were carried out by this method. The properties of the substances prepared are shown in the table.

Synthesis of N-(alkoxymethyl)lactams

Compound No.	Yield, %	$n_D^{20}$	$d_4^{20}$	MR		Found, %			Calculated, %		
				found	calculated	C	H	N	C	H	N
I	64,5	1,4618	1,088	32,55	33,30	55,75 55,68	8,68 8,52	10,45 10,59	55,79	8,50	10,7
II	58,6	1,4583	1,0502	37,15	37,91	58,73 58,99	9,30 9,46	9,85 9,92	58,71	19,15	9,79
III	58,63	1,4598	1,0104	46,39	47,15	62,74 62,72	10,10 10,01	8,42 8,51	63,12	10,09	8,18
IV	59,2	1,4702	1,0007	56,02	56,39	65,80 65,85	10,28 10,38	7,21 7,25	66,30	10,0	7,03

The reaction of N-(chloromethyl)pyrrolidone with butyl alcohol (in the absence of alcoholate). 25.9 g of butyl alcohol was placed in a three necked flask with a stirrer and 9.8 g of N-(chloromethyl)pyrrolidone was added through a dropping funnel. The reaction was slightly exothermic and the temperature increased from 24 to 32°. The reaction mixture was heated on a water bath at 50-55° for two hours, and simultaneously a stream of nitrogen was blown through in order to remove hydrogen chloride. The HCl was passed through a T'shchenko flask filled with water. The HCl content of the flask was determined by titration (32%). After distilling off the butyl alcohol N-(butoxymethyl)pyrrolidone was obtained; b. p. 75-76° (0.9 mm);  $n_D^{20}$  1.4574;  $d_4^{20}$  1.0043; MR 46.16; yield 41.5%.

The hydrolysis of N-(butoxymethyl)caprolactam. 4.5 g of N-(butoxymethyl)- $\epsilon$ -caprolactam and 30 ml of 2%  $H_2SO_4$  were placed in a three-necked flask and the mixture heated to 70-75° while passing a current of nitrogen through it. The gas given off was collected in Tishchenko flasks filled with water. By means of titration the presence of 2% of formaldehyde was determined. The reaction mixture was neutralized with  $BaCO_3$ . The filtrate was separated from the precipitate, and distilled. From the first fraction, b. p. 116.2°, after salting out with potash, 1.3 g of butyl alcohol,  $n_D^{20}$  1.3996, were obtained. The product remaining in the distillation flask was  $\epsilon$ -caprolactam, m. p. 63-64.5°.

The reaction of N-( $\beta$ -chloroethyl)- $\alpha$ -pyrrolidone with an alcoholic solution of sodium methylate. 5.6 g of N-( $\beta$ -chloroethyl)- $\alpha$ -pyrrolidone was added drop by drop to sodium methylate prepared from 9.7 g of methanol and 0.87 g of metallic sodium. With the addition of the first drops of chloride to the reaction mixture, a white precipitate of NaCl was observed. After the addition of all the chloride, the reaction mixture was heated to 45-48° with stirring for 25-30 minutes. The precipitate was filtered off and washed with diethyl ether, and the filtrate treated as in the preparation of N-(butoxymethyl)- $\alpha$ -pyrrolidone in the absence of alcoholate. After fractionation, 2.7 g of vinylpyrrolidone, b. p. 61.5-62° (1 mm),  $n_D^{20}$  1.5124, were obtained. By titration with iodoform, the vinylpyrrolidone content of the reaction mixture was found to be 85%. Spectroscopic analysis (UV spectra) confirmed the presence of N-vinylpyrrolidone since ~100% content of vinylpyrrolidone was found in the reaction mixture.



The reaction of N-( $\beta$ -chloroethyl)pyrrolidone with an alcoholic solution of sodium butylate. 5.9 g of N-( $\beta$ -chloroethyl)pyrrolidone was added drop by drop to sodium butylate prepared from 23.7 g of butyl alcohol and 0.92 g of metallic sodium and heated to 35°; a precipitate was observed to fall. The addition of N-( $\beta$ -chloroethyl)pyrrolidone was carried out in the course of 30 minutes at a temperature of 33-37°. After the addition of all the chloride, heating and stirring were continued for another 25-30 minutes. The products were worked up just as in the preceding experiment. After removing the benzene and distilling (using an oil pump) 7.0 g of N-vinylpyrrolidone were obtained which, after double redistillation, had b. p. 65-67° (1.5 mm),  $n_D^{20}$  1.5125.

The reaction of butyl bromide with the alcoholate of N-( $\beta$ -hydroxyethyl)pyrrolidone. 10.25 g of butyl bromide was slowly added through a dropping funnel to the alcoholate which was prepared from 1.72 g of Na and 21 g of N-( $\beta$ -hydroxyethyl)pyrrolidone. This was heated for 2-2.5 hours at 100-102° and the formation of a precipitate was noted. The precipitate was filtered off and extracted with dioxane. The filtrate, combined with the extract, was distilled in vacuo. 24.9 g of N-( $\beta$ -butoxyethyl)pyrrolidone were obtained; b. p. 68-81° ( $3 \cdot 10^{-2}$  mm),  $n_D^{20}$  1.4640. After supplementary purification it showed: b. p. 76-78° (1 mm),  $n_D^{20}$  1.4644. Found: C 63.28, H 10.62, N 7.38%.  $C_{10}H_{19}NO_2$ . Calculated: C 63.38, H 10.35, N 7.68%.

The reaction of ethyl bromide with the alcoholate of N-( $\beta$ -hydroxyethyl)pyrrolidone. Under the conditions of the previous experiment, 8.2 g of ethyl bromide was added to alcoholate prepared from 1.72 g of metallic sodium and 15.5 g of N-( $\beta$ -hydroxyethyl)pyrrolidone. The precipitate was filtered off, washed with dioxane, and the filtrate distilled in vacuo. 6.2 g of N-( $\beta$ -ethoxyethyl)pyrrolidone was obtained; b. p. 95-109° (1 mm),  $n_D^{20}$  1.4638, yield 52%. After redistilling three times the b. p. was 99-100° (1 mm),  $n_D^{20}$  1.4644;  $d_4^{20}$  1.0388. Found: C 59.98, 59.85; H 9.52, 9.45; N 9.32, 9.24%; MR 41.78.  $C_8H_{15}NO_2$ . Calculated: C 61.12, H 9.61, N 9.54%; MR 41.54.

#### SUMMARY

1. The reaction of N-chloromethylactams with alcohols was studied. N-(alkoxymethyl)pyrrolidones and N-(alkoxymethyl)caprolactams were synthesized. The compounds synthesized were easily hydrolyzed by dilute acid.
2. In the reaction of N-( $\beta$ -chloroethyl)pyrrolidone and an alcoholic solution of alcoholate, in distinction from acid analogs and also from  $\alpha$ -chloroalkylactams, detachment of HCl occurs instead of the substitution of an atom of chlorine by an alkoxy group.
3. N-( $\beta$ -alkoxyethyl)pyrrolidones were synthesized by the reaction of alkyl bromides with the alcoholate of N-( $\beta$ -hydroxyethyl)pyrrolidone.

#### LITERATURE CITED

1. M. F. Shostakovskii, F. P. Sidel'kovskaya, and M. G. Zelenskaya, *Izv. AN SSSR, Otd. Khim. Nauk* **1957**, 1457; *Vestnik AN SSSR*, No. 7, 45 (1957).
2. M. F. Shostakovskii, F. P. Sidel'kovskaya, and A. M. Khomutov, *Izv. AN SSSR, Otd. Khim. Nauk* **1955**, 919.
3. W. Reppe, *Polyvinylpyrrolidone*, Verlag Chemie, Weinheim, 1954.
4. M. F. Shostakovskii and F. P. Sidel'kovskaya, *Izv. AN SSSR, Otd. Khim. Nauk* **1958**, 111.
5. F. P. Sidel'kovskaya, M. G. Zelenskaya, and M. F. Shostakovskii, *Izv. AN SSSR, Otd. Khim. Nauk* **1959**, 901.
6. M. F. Shostakovskii, F. P. Sidel'kovskaya, and M. G. Zelenskaya, *Izv. AN SSSR, Otd. Khim. Nauk* **1961**, 910.
7. Kamo, Kōrē karaky dzaccu, *J. Chem. Soc. Japan Industry Chem. Soc.* **60**, N 4, 421 (1957); *RZhKhim*, No. 8, 25110 (1958).
8. M. F. Shostakovskii, *Simple Vinyl Ethers*, *Izd. AN SSSR*, M (1952) [in Russian].
9. M. F. Shostakovskii and F. P. Sidel'kovskaya, *Zh. obshch. khimii* **24**, 1576 (1954).
10. B. Puetzer, L. Katz, and L. Horwitz, *J. Amer. Chem. Soc.* **74**, 4959 (1952).

# STUDIES OF THE CHEMICAL CONVERSIONS OF UNSATURATED AND HIGH MOLECULAR WEIGHT COMPOUNDS

## COMMUNICATION 19. ALTERNATION DURING COPOLYMERIZATION OF VINYL ETHERS.

A. M. Khomutov

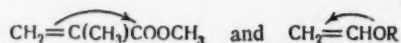
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Original article submitted June 24, 1960

In accordance with present concepts, copolymerization of monomers proceeds in such a way that the more active monomer enters the copolymer with relatively greater velocity than the less active monomer. The behavior of monomers on copolymerization, however, is not determined by their activity alone; many monomers have a tendency toward alternation [1]. The alternation effect is related to the polarity of the monomers and the interacting radical [2]. Substituents of ethylene, by giving up or attracting electrons of the C=C bond to a greater or lesser degree, may play a role either as electron donors or as electron acceptors. Depending on the properties of the substituent, the double bond of the monomer may be either more "positive" or more "negative." The greater the difference in polarity or in electron donor-acceptor properties between two monomers, the greater is their tendency toward alternation [2]. Therefore in the copolymerization of methyl methacrylate with vinylalkyl ethers, the alternation effect must be considerable since the alkoxy group of the vinyl ethers is an electron donor and the double bond will be "negative," while the double bond of methyl methacrylate is considered "positive," i.e., the two monomers have a structure which should permit alternation.



The tendency toward alternation of these monomers is confirmed by the product of their constants of copolymerization  $r_1 \cdot r_2 = 1.6 \cdot 0 \approx 0$  [3]. In case the alternation effect is complete, the relationship between yields, composition and concentration of the original monomers may be shown graphically (Fig. 1), i.e., with increasing concentration of the vinyl ether in the reaction medium, the composition of the copolymer remains constant (50 mole %); yields increase, reaching a maximum with an equimolecular ratio of the original monomers, and then decrease. However the experiment did not confirm whether or not a relationship of the following order exists between yields, composition and concentration of the monomers. With increasing concentration of the vinyl ethers in the reaction medium, the yields of copolymers decrease and the number of vinyl ether molecules in them increases [4]. The alternation effect is reduced because of the concentration and activity of the acrylates which have a conjugated double bond. Our studies showed that owing to an increase in the concentration of vinyl ether in the reaction medium, it is possible to exclude the effect of the activity of the acrylates and consider only the effect of alternation [5]. In connection with this the opposite thought occurred: owing to the increase in concentration of the active acrylate, to exclude the alternation effect during copolymerization, and to investigate the possibility of growth only of the polymeric chain of the active acrylate. In order to verify this supposition, the copolymerization reaction was carried out in the presence of an excess of methyl methacrylate (75 mole %) and 25 mole % of vinylbutyl ether. When the reaction was stopped after eight hours, and after fractionating the polymers formed, not only was the copolymer of methyl methacrylate and vinylbutyl ether obtained, but also the polymer of methyl methacrylate. The yields and composition of the fractions are shown in Table 1.

Fraction I is a polymer of methyl methacrylate, thus confirming the possibility of the appearance of the alternation effect at some stage of the copolymerization reaction. It should be noted that on continuing the reaction for 40 hr, it was not possible to obtain the polymer [5]. Thus, at the beginning of the process the influence of the concentration of the methyl methacrylate in the reaction medium is significant; when the concentration of the second component, vinylbutyl ether, increases, the alternation effect is observed and the monomer of vinylbutyl ether

combines with a radical of the polymeric chain of methyl methacrylate. In order to find the rate of consumption of the monomers, experiments were undertaken to determine the rate of formation of the polymeric chain in relation to time and concentration of the original monomers. For this purpose 75 mole % of methyl methacrylate and 25 mole % of vinylbutyl ether and, conversely, 25 mole % of methyl methacrylate and 75 mole % of vinylbutyl ether were copolymerized. Tests were taken every hour. The yields and composition of the polymerization products were determined. The influence of reaction time on the content of chains of vinyl ethers in the copolymer is shown in Fig. 2.

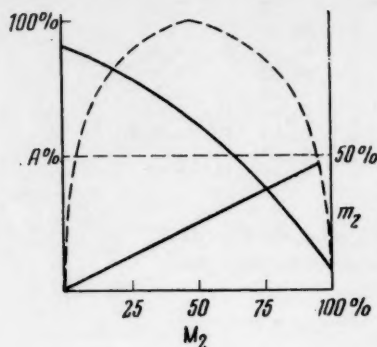


Fig. 1. The influence of the concentration of monomers on the yield and composition of copolymers: A) yields of copolymers in percent;  $M_2$ ) initial concentration of the monomer in mole %;  $m_2$ ) number of molecules chains of vinyl ether in the copolymer in mole %.

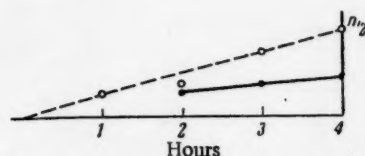


Fig. 2. Reaction rate of the copolymerization of methyl methacrylate and vinylbutyl ether.  $m_2$ ) quantity of vinylbutyl ether chains in the copolymer in mole %; ○) 75 mole % of vinylbutyl ether and 25 mole % of methyl methacrylate; ●) 75 mole % of methyl methacrylate and 25 mole % of vinylbutyl ether.

weight at 20-25° and analyzed for its carbon and hydrogen content. The relative viscosity of acetone solutions of the copolymers was also determined. The first fraction was subsequently refractionated to separate the polymer of methyl methacrylate. Experimental data are shown in Table 1.

**Rate of copolymerization.** A study of the rate of copolymerization of methyl methacrylate and vinylbutyl ether in the presence of benzene peroxide was carried out in two concentrations of the original monomers: a) methyl methacrylate 75 and 25 mole %; b) vinylbutyl ether 75 and 25 mole %. 75 mole % of methyl methacrylate and 25 mole % of vinylbutyl ether were placed in sealed ampoules. The conditions for copolymerization were described above. The ampoules were removed from the thermostat every hour. Then the contents of the ampoule were cooled, transferred to a flask, and treated with petroleum ether until the monomer was completely removed. The separated polymeric products were analyzed. Experimental data are shown in Table 2.

From Fig. 2 it is evident that during the first hour in the presence of an excess of methyl methacrylate, only its own polymer was formed, and then, as the concentration of the vinyl ether increased, alternation of the monomeric chains set in and the copolymer was formed. If the reaction is allowed to proceed in the presence of an excess of a less active vinylbutyl ether, the tendency of the monomers toward alternation begins to appear from the beginning of growth of the polymeric chain. Thus, the formation of a polymer of methyl methacrylate in the presence of an excess of its monomer in the reaction medium was confirmed, and the influence of the concentration of the original monomers on the alternation effect during copolymerization was shown.

## EXPERIMENTAL

The original substances had the following properties: methyl ester of methacrylic acid, b. p. 100°,  $n_D^{20}$  1.4160;  $d_4^{20}$  0.936; vinyl n-butyl ether, b. p. 33.7-33.8°,  $n_D^{20}$  1.4026;  $d_4^{20}$  0.7782. The copolymerization reaction was carried out in ampoules at a temperature of  $60 \pm 1^\circ$ . The quantity of initiator (benzene peroxide) used was 0.2% of the total weight of the original monomers. The length of the experiments was determined by the reaction conditions. After stopping the copolymerization reaction the ampoules were cooled by a mixture of acetone and solid carbon dioxide. The way in which the copolymers were processed depended upon the purpose of each experiment.

**Fractionation of copolymers.** After heating methyl methacrylate (75 mole %) and vinylbutyl ether (25 mole %) for eight hours, the ampoules were opened, acetone was added and the polymeric product reprecipitated several times by means of methanol until the reaction for a double bond was negative. The polymeric product was transferred to a flask, and dried to constant weight at 20° at 1 mm; 10 g of this polymer was dissolved in 250 ml of acetone; fractionation of the polymer was done by means of methanol. The first fraction was separated after the addition of 250 ml of methanol to a solution of it. The copolymer was removed from the solution, and further fractionation was carried out by the addition of 100 ml portions of methanol. The last fraction was dried to constant

TABLE 1. Composition and Yields of Fractions of Copolymers of Vinylbutyl Ether (I) and Methyl Methacrylate (II)

Fraction	Yield, %	Molecular composition of the copolymers, %		% C found in copolymer	$\eta$ (rel)
First subfraction	9,0	—	100	59,8	—
Second subfraction	31,4	1,7	98,3	60,16	3,66
II	17,9	2,65	97,35	60,32	2,96
III	10,4	2,25	97,75	60,27	2,4
IV	1,8	9,17	90,83	61,10	2,05
V	13,8	8,44	91,66	61,10	1,97
VI	3,9	14,0	86,0	61,68	—
VII	11,6	17,6	82,4	62,11	1,56

TABLE 2. Rate of Copolymerization of 75 mole % of Methyl Methacrylate (I) and 25 mole % of Vinylbutyl Ether (II) in the Presence of Benzene Peroxide

Length of reaction, min	Yield, %	% C found in copolymer	Molecular composition of copolymer, %		$\eta$ (rel)
			(I)	(II)	
60	1,0	59,66	100	—	2,024
120	4,98	60,83	93,0	3,0	2,415
180	8,47	61,0	91,7	8,3	2,243
240	8,88	61,17	90,25	9,75	2,139

TABLE 3. Rate of Copolymerization of 25 mole % of Methyl Methacrylate (I) and 75 mole % of Vinylbutyl Ether (II) in the Presence of Benzene Peroxide

Length of reaction, min	Yield, %	% C found in copolymer	Molecular composition of copolymer, %		$\eta$ (rel)
			(I)	(II)	
60	0,22	60,65	94,58	5,42	—
120	0,46	60,89	92,58	7,42	—
180	2,25	61,84	84,7	15,3	1,792
240	2,70	62,50	79,1	20,9	1,726

Copolymerization of a mixture of 25 mole % of methyl methacrylate and 75 mole % of vinylbutyl ether was carried out under the same conditions. Experimental data are shown in Table 3.

#### SUMMARY

The concentration of the original monomers in the reaction medium influences the alternation effect during the copolymerization of vinyl ethers with acrylates. A concentration of the active monomer may be chosen such that the polymer of methyl methacrylate will be formed at the beginning.

#### LITERATURE CITED

1. T. Alfrey and others, Copolymerization, IL (1953) p. 50 [in Russian].
2. F. Lewis, F. Mago, and C. Walling, J. Amer. Chem. Soc. **70**, 1529 (1948).
3. S. N. Ushakov, S. P. Mitsengendler, and G. A. Shtraikhman, Uspekhi khimii **19**, 281 (1950).
4. A. M. Khomutov, Dissertation (Moscow, 1954).
5. A. M. Khomutov, Izv. AN SSSR, Otd. Khim. Nauk **1961**, 352.



# CATALYTIC HYDROGENATION OF DIMETHYLVINYLETHYNYLCARBINOL

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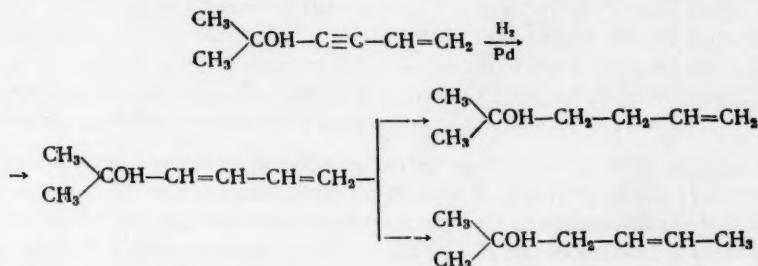
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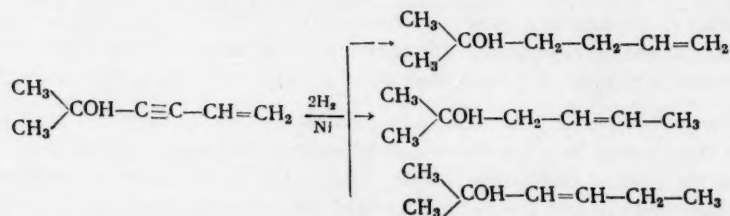
Original article submitted July 11, 1960

The preparation of dienes by the selective catalytic hydrogenation of the more available vinylacetylene compounds is of considerable interest. The selective reduction of vinylacetylene hydrocarbons and alcohols, especially dimethylvinylethynylcarbinol, has attracted the greatest attention from investigators. Zonis [1] assumed that, in the presence of palladium precipitated on starch or barium carbonate, dimethylvinylethynylcarbinol would be selectively hydrogenated to the diene alcohol 5-methylhexadiene-1,3-ol-5. The product obtained had b. p. 50-51° (12 mm);  $n_D^{20}$  1.45668;  $d_4^{20}$  0.85805, and in the presence of platinum black absorbed two moles of hydrogen. Nazarov and Fisher [2] showed that, on hydrogenation in the presence of palladium on calcium carbonate under the same conditions, after the absorption of one mole of hydrogen, there is formed not a diene alcohol, but a complex mixture consisting of the original dimethylvinylethynylcarbinol (~30%), a diene alcohol (~40%) and ethylene alcohols (~30%). The structure of these alcohols was established by ozonization. Thus, the reaction does not proceed selectively: the diene alcohol formed is hydrogenated simultaneously with the dimethylvinylethynylcarbinol



Similar results were obtained by Bal'yan [3] in the presence of colloidal palladium. The content of unreacted carbinol in the products of catalysis was determined by the quantity of vinylacetylene separated out by the action of metallic sodium. An effort to increase the selective action of the palladium catalyst by the addition of p-thiocyanobenzene or p-thiocyananiline was not effective.

A mixture of ethylene alcohols was formed by the combination of two moles of hydrogen in the presence of a nickel catalyst [2].



A complex mixture was obtained from the reaction with one mole of hydrogen, the composition of which was not studied. The electrolytic reduction of dimethylvinylethynylcarbinol also yields a complex mixture of products containing not less than 30-40% of diene alcohol [4]. Bates, Jones and Whiting [5] reduced dimethylvinylethynylcarbinol with lithium aluminum hydride in ether and stated that they obtained diene alcohol with a yield of 88%. We

noticed that the constants of the dimethyldivinylcarbinol obtained in this study [b. p. 55° (12 mm),  $n_D^{20}$  1.4758] were very close to those of the original carbinol, and so we repeated this reaction under the same conditions. It was found that the reduction product absorbed about three moles of hydrogen, and the lines 2233, 2214, 2117, 2108  $\text{cm}^{-1}$  which are characteristic of the  $\text{—C}\equiv\text{C—C=}$  system, were found in its infrared spectrum. In this case, apparently, the carbinol is not reduced at all.

Nazarov and Fisher stated that they had succeeded in accomplishing the selective reduction of dimethylvinylethynylcarbinol to 5-methyl-1,3-hexadiene-5 [b. p. 42-43° (9 mm),  $n_D^{20}$  1.4693,  $d_4^{20}$  0.8517] by the use of zinc-copper vapor and water [2]. Unlike dimethylvinylethynylcarbinol, the alcohol obtained slowly polymerized on standing, and benzene peroxide did not accelerate this process even on heating. On exhaustive hydrogenation this alcohol absorbed two moles of hydrogen. It is interesting to note that it was not possible to prepare an acetate with diene structure by the reduction of the acetate of dimethylvinylethynylcarbinol by the aid of copperized zinc dust and water, but that heptadiene was formed instead [6].

The present investigation was concerned with the possibility of preparing diene alcohol by the partial hydrogenation of this carbinol using a nickel catalyst poisoned by pyridine and a zinc catalyst which had shown selective action in the hydrogenation of enyne hydrocarbons to dienes [7].

## EXPERIMENTAL

The hydrogenation over nickel was carried out in a rotating autoclave (volume 0.5 liters) with the absorption of one, two or three moles of hydrogen, while the experiments at atmospheric pressure were carried out in a flask. Freshly vacuum-distilled dimethylvinylethynylcarbinol, b. p. 53-54° (9 mm) and  $n_D^{20}$  1.4778 was used. The nickel catalyst was prepared by alkalinizing finely pulverized 50% Ni-Al alloy (1:1) by means of a 20% solution of NaOH for two hours at 100°. The zinc catalyst was prepared by treating a (1:1) Zn:Al alloy with 3% NaOH at 75°. After alkalization the catalyst was washed with distilled water until it showed a neutral reaction with phenolphthalein. The reaction was carried out in a solution of methyl alcohol. After absorption of the required volume of hydrogen, the rotation of the autoclave was stopped, the excess hydrogen removed, the reaction products filtered off from the catalyst and the latter washed with methyl alcohol. The methanol solution was combined with the products of catalysis and distilled. After removal of the methanol, fractions were selected and their constants determined.

At the present time there are no methods for the quantitative determination of dimethylvinylethynylcarbinol and its hydrogenation products. Therefore in order to get some orientation on the character of the fractions obtained, their carbinol content was determined by the quantity of vinylacetylene given off by the action of metallic sodium [3]. Preliminary experiments showed that it is possible to detect approximately 80% of the vinylacetylene (and not 90-92%, as reported in [3]). The vinylacetylene was determined by gas-liquid chromatography, and the results obtained coincided with those obtained by absorption of vinylacetylene in an alkaline solution of  $\text{K}_2\text{HgI}_2$ . The curves showing the kinetics of hydrogenation of these fractions were compared with that of the hydrogenation of the original carbinol. A study of the rate of hydrogenation of dimethylvinylethynylcarbinol and of the fractions obtained was carried out over a nickel catalyst in a solution of methanol or ethanol (96%) at 25° and with 700 oscillations of the flask per minute. Readings of the volume of hydrogen used were taken every 30 seconds. The resulting curves show a dependence of the rate of reaction ( $\Delta V/\Delta t$ ) on the volume of hydrogen absorbed ( $\Sigma V/2$ ).

The hydrogenation of dimethylvinylethynylcarbinol in the presence of a nickel catalyst. Table 1 shows the conditions and results of the experiments on the hydrogenation of dimethylvinylethynylcarbinol over a nickel catalyst at atmospheric pressure and under pressure. The constants of the product obtained from the absorption of three moles of hydrogen correspond with those of 2-methylhexanol-2  $(\text{CH}_3)_2\text{COH—CH}_2\text{—CH}_2\text{—CH}_2\text{—CH}_3$  [8].

Figure 1 shows the curves for exhaustive hydrogenation over nickel in methyl alcohol (curve 1) or ethyl alcohol (curve 2) at 25°. These curves have two characteristic portions. In portion I approximately two moles of hydrogen are absorbed. One may assume that basically what occurs in this portion is the hydrogenation of a triple and a conjugated double bond, and in portion II — hydrogenation of the ethylene alcohol which has been formed. This is confirmed by the fact that after two moles of hydrogen have been absorbed, ethylene alcohol is formed. If we start with the data of [2], the constants of the product (Table 1) are found to be close to the constants of a mixture of isomeric ethylene alcohols (I) — (III), while according to the data of [9], they correspond with the properties of alcohol (I). In Fig. 1, curve 3 shows the hydrogenation of this product. As can be seen, the shape of the curve corresponds with the shape of the curve for the hydrogenation of the original carbinol in portion (II) after the point of inflexion (Fig. 1, curve 2). In the following experiments the addition of one mole of hydrogen to dimethylvinylethynyl-

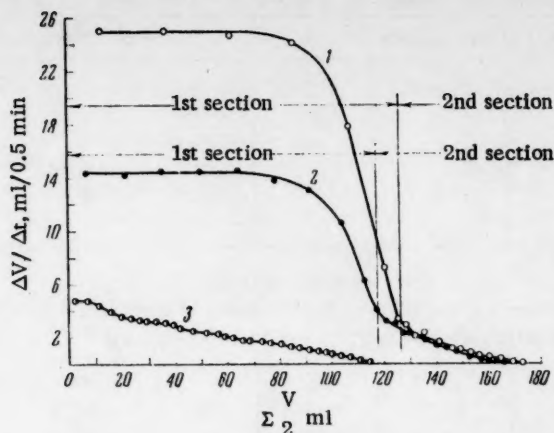


Fig. 1. Hydrogenation of dimethylvinylethynylcarbinol (curves 1-2) and dimethylbutenylcarbinol (curve 3) over a nickel catalyst at 25°. 1) 0.2574 g in 10 ml  $\text{CH}_3\text{OH}$ ; 2) 0.2402 in 10 ml of  $\text{C}_2\text{H}_5\text{OH}$ ; 3) 0.7134 g in 10 ml of  $\text{C}_2\text{H}_5\text{OH}$ .

TABLE 1. Hydrogenation of Dimethylvinylethynylcarbinol Over a Nickel Catalyst at 25° with the Absorption of Two or Three Moles of Hydrogen

	Addition of hydrogen			
	two moles		three moles	
	at atmos. press.	under press.	at atmos. press.	under press.
Experimental conditions				
Quantity of dimethylvinylethynylcarbinol, ml	10	50	10	50
Wt. of catalyst, g	2	5	2	5
Solvent, ml	$\text{CH}_3\text{OH}$ , 50	$\text{CH}_3\text{OH}$ , 50	$\text{CH}_3\text{OH}$ , 50 piperidine	$\text{CH}_3\text{OH}$ , 50 pyridine
Pressure, atm	—	84	—	82
Properties of product obtained				
Boiling point, °C (in mm)	140.9-141.3 (740)	141-142 (740)	137-138 (750)	136-138 (745)
$n_D^{20}$ (t)	1.4198 (19°)	1.4200 (19.3°)	1.4367 (19.5°)	1.4362 (19.8°)
$d_4^{20}$	0.8139	0.8153	0.8349	0.8392

carbinol was studied. Reaction conditions, properties of the fractions separated from the products of catalysis and the results of experiments on the determination of the degree of unsaturation of the latter, are shown in Table 2. Figures 2-4 show the curves of the hydrogenation of these fractions.

The magnitudes of the indices of refraction of fractions I-II, obtained in the experiment at atmospheric pressure (Table 2, Expt. 1), the over-all consumption of hydrogen, and the volume of hydrogen absorbed up to the point of inflexion on the curves, show that these fractions along with diene alcohol (~ 40-50%), also contain ethylene alcohol. The same factors indicate that fractions III and IV contain more diene alcohol and an admixture of the original carbinol, while fraction V contains the original carbinol. From Fig. 2 it can be seen that the horizontal portion is missing from the curves on the hydrogenation of fractions I and II (curves 1 and 2). On the other hand the hydrogenation curves of fractions III and IV (curves 3 and 4) have a horizontal portion which indicates that they contain triple and conjugated double bonds. As a matter of fact, 15% of carbinol was determined in fraction III by

TABLE 2. Hydrogenation of Dimethylvinylethynylcarbinol with the Absorption of One Mole of Hydrogen

Expt.	Properties of the product				Determ. of unsaturation of prods. obtained				
	Fraction No.	B. p. °C (press. in mm)	Quantity, g	$n_D^{20}$	Carbinol content of fraction, %	wt. of frac. sample, g	Consumption of H <sub>2</sub> based on diene alcohol, ml		Vol. of H <sub>2</sub> absorbed up to the point of inflexion on the kinetic curve, ml
							theor.	fact.	

## Over a nickel catalyst

[wt. of catalyst - 3 g; quantity of carbinol - 50 ml; volume of methanol - 50 ml; temperature - 25°; atmospheric pressure (expt. 1) and 70 atm (expt. 2)]

1	I	44-45 (11)	1.6*	1.4439	0	0.3563	164	106	41
	II	46.5-50 (11)	11.0*	1.4464	0	0.3634	171	129	56
	III	50-53.3 (11)	6.7*	1.4540	15	0.3657	168	148	85
	IV	53.5-56 (11)	9.0*	1.4599	-	0.3684	169	194	133
	V	> 56 (11)	1.3*	1.4748	-	0.2944	203	184	134
2	I	To 46 (9)	16.0*	1.4504	0	0.3735	173	138	69
	II	46-48 (9)	13.0*	1.4570	19	0.3778	175	171	108
	III	49 (9)	2.0*	1.4670	-	-	-	-	-
	IV	> 49 (9)	10.0*	1.4779	-	-	-	-	-

## Over a nickel catalyst in the presence of pyridine

(wt. of catalyst - 3 g; wt. of carbinol - 44.1 g; volume of methanol - 25 ml; volume of pyridine - 25 ml; temperature - 25°; pressure - 70 atm.)

3	I	48.5-51 (19)	16.84	1.4563	8	0.2325	104	117***	48
	II	53-57.5 (19)	15.37	1.4534					
	III	59 (18-19)	5.81	1.4636	36	0.3676	166	195***	121
	IV	59 (18-19)	3.57	1.4787	-	-	-	-	-

## Over a zinc catalyst

(volume of catalyst - 50 ml; wt. of carbinol - 42.8 g; volume of methanol - 50 ml; temperature 100°; pressure - 100 atm.)

4	I	51-56 (19)	3.32	1.4517	2	0.3203	143	96	46
	II	56.5-57.5 (19)	32.26	1.4656	10	0.3870	173	178	114
	III	57.5 (19)	1.2	1.4765	-	0.1909	131**	122	85
	IV	Tar	0.5	-	-	-	-	-	-

\*Vol. in milliliters.

\*\*Calculated on original carbinol.

\*\*\*On an activated rhodium catalyst.

method [3]. Judging by the index of refraction, approximately the same amount of unreacted carbinol is to be found in fraction IV. The hydrogenation curve of fraction V (Fig. 2, curve 5) is analogous to that of the hydrogenation curve of the original carbinol (Fig. 1, curve 1). Similar results were obtained on the hydrogenation of dimethylvinylethynylcarbinol under pressure (Table 2, expt. 2); fraction I (Fig. 2, curve 6) consists basically of diene alcohol with an admixture of ethylene alcohol, while fraction II (Fig. 2, curve 7) consists of a mixture of diene alcohol and the original carbinol. Thus, in the presence of a nickel catalyst, both at normal and elevated pressures, the total quantity of diene alcohol in the products of catalysis probably does not exceed 50%.

It was pointed out previously that the rate of hydrogenation of hydrocarbons containing conjugated double bonds [10, 11] over nickel in the presence of pyridine is greatly reduced. In this connection an effort was made to increase the yield of diene alcohol by means of the partial hydrogenation of dimethylvinylethynylcarbinol in the presence of



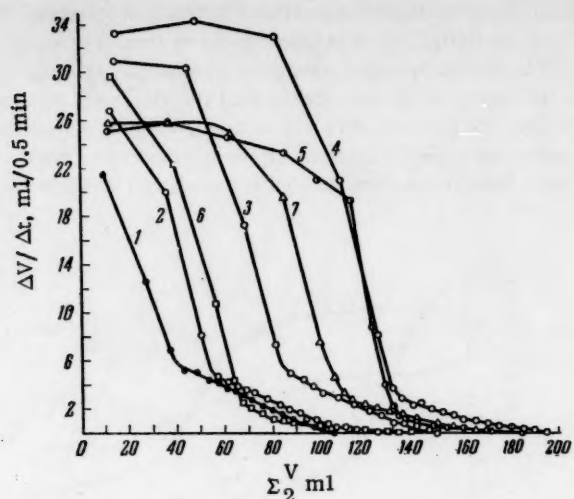


Fig. 2. Hydrogenation of fractions obtained by the distillation of the products of catalysis of experiment I (curves 1-5) and experiment 2 (curves 6-7), over a nickel catalyst in  $\text{CH}_3\text{OH}$ : curves 1 and 6 - fraction I; curves 2 and 7 - fraction II; curve 3 - fraction III; curve 4 - fraction IV; curve 5 - fraction V.

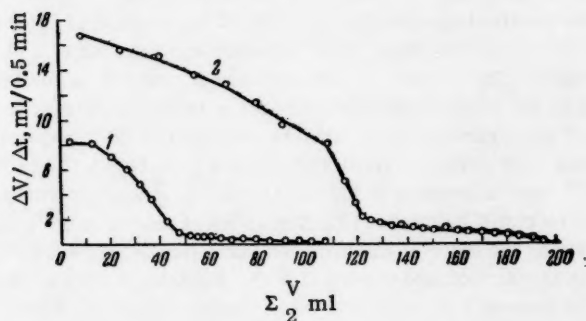


Fig. 3. Hydrogenation of fractions obtained by the distillation of the products of catalysis of experiment 3, over a nickel catalyst in  $\text{C}_2\text{H}_5\text{OH}$ : 1) fractions I-II; 2) fraction III.

pyridine. The results of these experiments are presented in Table 2 (experiment 3) and are shown in Fig. 3. Fractions I and II were combined, and on hydrogenation 0.2325 g of this product absorbed  $\sim 117$  ml of hydrogen as against 104 ml which would be necessary on calculation for diene alcohol. The shape of the hydrogenation curve (Fig. 3, curve 1) indicates the presence of an admixture of the original carbinol. Eight percent (2.6 g) of the latter was detected in it by method [3]. By comparison of the hydrogenation curve of fraction III (Fig. 3, curve 2) with the hydrogenation curve of the original dimethylvinylethynylcarbinol (Fig. 1, curve 2) it can be seen that fraction III contains a considerable quantity of the original carbinol. Thirty-six percent (2.1 g) of dimethylvinylethynylcarbinol was found in fraction III by method [3]. As is evident from the index of refraction, fraction IV (3.6 g) is the original carbinol (Table 2, experiment 3). Thus in experiment 5 the products of catalysis contain  $\sim 8.2$  g ( $\sim 19\%$ ) of dimethylvinylethynylcarbinol. Consequently, on absorption of one mole of hydrogen, the products of catalysis of experiment 3 contain just the same amount of ethylene alcohol. Hence the yield of diene alcohol (taking losses into account) reached  $\sim 57\%$ . Therefore poisoning the nickel catalyst with pyridine does not result in any significant increase in the yield of diene alcohol.

The hydrogenation of dimethylvinylethynylcarbinol over a zinc catalyst. The experiments were carried out at a temperature of 100° and an initial hydrogen pressure of 100 atm. The volume of catalyst was 50 ml; the volume of methanol 50 ml. The rate of hydrogen absorption was considerably less than in the case of hydrogenation over nickel, and the reaction ceased of its own accord after the absorption of approximately two moles of hydrogen. After distilling off the solvent, the products of catalysis distilled almost completely at 50-51° (12 mm);  $n_D^{20}$  1.4370;  $d_4^{20}$  0.8345. These properties correspond with those of dimethylbutenylcarbinol. Thus, over a zinc catalyst, the reaction ceases at the stage where an ethylene alcohol is formed and no further hydrogenation occurs.

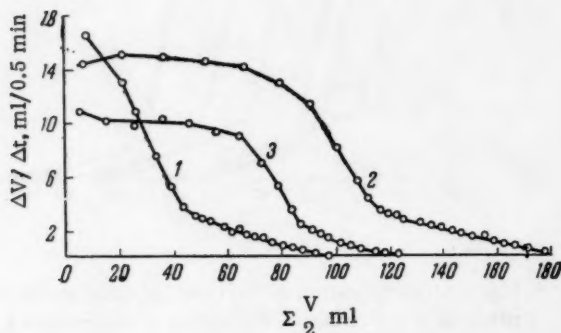


Fig. 4. Hydrogenation of fractions obtained by the distillation of the products of catalysis of experiment 4, over nickel in  $C_2H_5OH$ : 1) fraction I; 2) fraction II; 3) fraction III.

Table 2 shows the results of experiments on the addition of one mole of hydrogen to dimethylvinylethynylcarbinol. As can be seen from the results of the distillation, ~75% of the products of catalysis are found in fraction II, which boils within the limits 56.5-57.5° (19 mm), has  $n_D^{20}$  1.4656 and is basically a diene alcohol. The shape of the hydrogenation curve of fraction II (Fig. 4, curve 2) indicates that it contains an admixture of the original carbinol. On the portion of the curve up to the point of inflexion ~114 ml of hydrogen were absorbed instead of the 86 ml calculated for the hydrogenation of diene carbinol to an ethylene carbinol (Table 2, experiment 4). The following frequencies occur in the combination light dispersion spectra of fraction II: 2215 (6), 2147 (0), 2108 (1), 1615 (9), 1594 (3), 1552 (0)  $cm^{-1}$ ; the 2215  $cm^{-1}$  line corresponds to the  $-C \equiv C - C = C$  group. Approximately 10% (3.2 g) of the original carbinol was found in fraction II by method [3]. The index of refraction ( $n_D^{20}$  1.4765), the consumption of hydrogen (Table 2, experiment 4) and the shape of the hydrogen curve (Fig. 4, curve 3) of fraction III correspond with those of the original carbinol; its yield amounted to ~4% (1.7 g). A small quantity of dimethylvinylethynylcarbinol (~2%) (0.1 g) was also found in fraction I; its yield was ~8%. On hydrogenating 0.3203 g of this fraction, 96 ml of hydrogen was absorbed, or ~70% calculated on the diene carbinol. This also indicates the presence of ethylene alcohol in it, which is also confirmed by the shape of the hydrogenation curve of this fraction (Fig. 4, curve 1). Judging by the consumption of hydrogen up to the point of inflexion on the curve, fraction I contains no more than 50-60% of the diene carbinol.

The data presented show that altogether the products of catalysis contain ~5g of dimethylvinylethynylcarbinol, which amounts to ~12% of the carbinol originally taken for hydrogenation. Thus, on hydrogenating dimethylvinylethynylcarbinol over a zinc catalyst, after the absorption of a mole of hydrogen, there is also formed a complex mixture consisting of the original carbinol (~15%), diene alcohol (~70%) of ethylene alcohol (~15%).

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#### SUMMARY

1. In the presence of a nickel catalyst the addition of one mole of hydrogen to dimethylvinylethynylcarbinol proceeds nonselectively: a mixture is formed that contains the original carbinol and diene and ethylene alcohols. Partial blocking of the surface of the catalyst by means of pyridine did not lead to any significant increase in the yield of diene alcohol.

2. In the presence of a zinc catalyst dimethylvinylethynylcarbinol is selectively hydrogenated to dimethylbutenylcarbinol. After the absorption of one mole of hydrogen the products of catalysis contain approximately 70% of diene alcohol. Thus, a zinc catalyst shows the greatest selectivity in this reaction.

#### LITERATURE CITED

1. S. A. Zonis, *Zh. obshch. khimii* **9**, 2191 (1939).
2. I. N. Nazarov and L. B. Fisher, *Izv. AN SSSR, Otd. Khim. Nauk* **1942**, 150.
3. Kh. V. Bal'yan, *Trudy Leningradskogo tekhnologicheskogo instituta im. Lensovetu*, (1957), No. 42, p. 10.
4. A. P. Golovchanskaya, *Zh. obshch. khimii* **8**, 435 (1940).
5. E. B. Bates, E. R. H. Jones, and M. C. Whiting, *J. Chem. Soc.* **1954**, 1954.
6. I. N. Nazarov and L. B. Fisher, *Izv. AN SSSR, Otd. Khim. Nauk* **1944**, 71.
7. L. Kh. Freidlin, V. I. Gorshkov, and T. K. Lavrovskaya, *Izv. AN SSSR, Otd. Khim. Nauk* **1959**, 2027.
8. G. Henry, *Chem. Zbl.* **1**, 1854 (1909).
9. K. Auwers and W. Moosbrugger, *Liebigs Ann. Chem.* **387**, 180 (1912).
10. L. Kh. Freidlin and B. D. Polkovnikov, *Izv. AN SSSR, Otd. Khim. Nauk* **1956**, 1502.
11. L. Kh. Freidlin, A. A. Balandin, I. F. Zhukova, and I. P. Yakovlev, *Izv. AN SSSR, Otd. Khim. Nauk* **1959**, 1640.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

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CATALYTIC HYDROCONDENSATION OF CARBON MONOXIDE WITH  
OLEFINS AND THEIR HYDROPOLYMERIZATION UNDER THE  
ACTION OF CARBON MONOXIDE AND HYDROGEN

COMMUNICATION 31. RELATION OF 2-METHYLBUTENE-1 AND 3,3-DIMETHYLBUTENE-1  
TO HYDROCONDENSATION CATALYSIS

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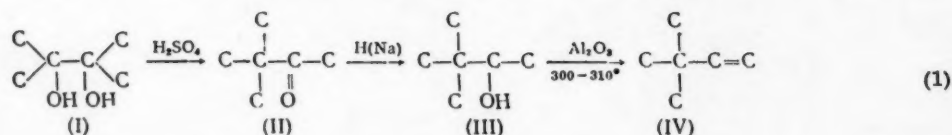
Conversions of the following  $C_5$ - and  $C_6$ -olefins under hydrocondensation catalytic conditions have been investigated previously: pentene-1 and pentene-2 [1], isopropylethylene [2], tri- and tetramethylethylene [3], and hexene-1 [4, 5]. It was shown that isoolefins at 190° and atmospheric pressure on a Co-clay Catalyst in hydrocondensation and hydropolymerization reactions reacted only to a small extent (5-10%) and were mainly hydrogenated to the corresponding paraffin hydrocarbon. In addition, in the case of isopropylethylene, double bond isomerization played a large part in its conversions. Unlike isoolefins,  $C_5$ - and  $C_6$ -olefins of normal structure participated more vigorously in the reactions indicated. Pentene-1 reacted to the extent of 28-30%, pentene-2 - 13-14%, hexene-1 - ~22%. In the case of pentene-1 and pentene-2, as in the case of isopropylethylene, double bond isomerization was observed chiefly from the  $\alpha$ - to the  $\beta$ -position. This reaction had been noted previously for n-butenes also [6]. Unlike the  $C_5$ - and  $C_6$ -isoolefins investigated, isobutylene actively participated in hydropolymerization and hydrocondensation reactions with CO, yield of liquid hydrocarbons amounting to ~60% on isobutylene passed [7, 8].

It was of interest to investigate 2-methylbutene-1 and 3,3-dimethylbutene-1 in the reactions indicated; the first of these has the structural element of isobutylene with regard to the double bond, the second is an  $\alpha$ -olefin incapable of double bond isomerization.

# EXPERIMENTAL

Initial 2-methylbutene-1 was synthesized by dehydrating isoamyl alcohol produced by fermentation (b. p. 129-132°;  $n_D^{20}$  1.4082;  $d_4^{20}$  0.8138) over  $Al_2O_3$  at 380-400°. The three isomeric pentenes obtained in this mixture after separation from water of reaction and drying over calcium chloride were fractionally distilled on a column packed with a three-cornered copper coil of effectiveness 60 theoretical plates. The 2-methylbutene-1 fraction with b. p. 29-32° was redistilled on the same column. The hydrocarbon thus obtained according to chromatographic analysis consisted of 97.6% 2-methylbutene-1, with 1.4% 3-methylbutene 1 and 0.8% 2-methylbutene-2, and had b. p. 31-32° (760 mm);  $n_D^{20}$  1.3780;  $d_4^{20}$  0.6501; MR found 24.83; MR calculated for  $C_5H_{10}$  24.78. Data in the literature [9]: p. 31.16;  $n_D^{20}$  1.3378;  $d_4^{20}$  0.6504.

Initial 3,3-dimethylbutene-1 was synthesized from pinacolone hydrate according to the scheme [10-12]:



In the last stage, on dehydrating pinacolone alcohol (III) a mixture of 3,3-dimethylbutene-1 (IV), 2,3-dimethylbutene-1, and 2,3-dimethylbutene-2 (tetramethylethylene) in the ratio ~1:0.6:0.2 was obtained, which was fractionated on the above-mentioned column. The fraction with b. p. 39-43° was redistilled, the fraction in the b. p.



range 41-42° (760 mm) being collected. The 3,3-dimethylbutene-1 obtained had  $d^{20}_4$  0.6526 and  $n^{20}_D$  1.3765; MR found 29.62; MR calculated for  $C_6H_{12}$  29.58. Data in the literature for 3,3-dimethylbutene-1 [9]: b. p. 41.24°;  $d^{20}_4$  0.6529;  $n^{20}_D$  1.3760.

Apparatus and procedure for carrying out the experiments did not differ from that described previously [13]. Experiments with each olefin were carried out at 190° and atmospheric pressure in a circulatory system, with previous by prepared Co-clay contact catalyst (1:2), the activity of which was checked during hydropolymerization of ethylene under the action of CO and was found to be high; yield of liquid hydropolymerizate amounted to 500-510 ml per cubic meter of initial gas of composition 40-50%  $C_2H_4$ , 4-5% CO, 45-50%  $H_2$ . Before each experiment the catalyst was regenerated with electrolytic hydrogen at 450°. The initial olefin was fed into a glass reaction tube of diameter 10 mm containing 30 ml of catalyst from an automatic burette at a fixed rate. The initial gas was simultaneously fed into the tube ( $H_2$  or a mixture of CO and  $H_2$ ). The catalyzate was collected in two receivers; in the first - at 15°, in the second - at 80°. After drying over calcium chloride and degasification by fractionation, the catalyzates were fractionally distilled up to a temperature of 84°. Fractionation residues were distilled from a small Wurtz flask. The resulting fractions were analyzed qualitatively by the method of Raman spectra. Evaluation of line intensity was carried out visually on a ten-division scale. Identification of spectra was obtained with the use of literature data on the Raman spectra of individual hydrocarbons [14]. Content of unsaturated products in the fractions and catalyzates were determined using their bromine numbers. Effluent reaction gases were analyzed thermochromatographically.

### Experiments with 2-Methylbutene-1

**2-Methylbutene-1.** Experiment 1 (Table 1) was carried out with 2-methylbutene-1 only in absence of gas-carrier. Before the experiment, the catalyst after reduction was treated with nitrogen (8 liters) to remove hydrogen from the system and the reaction zone. Then, to remove hydrogen from the catalyst surface, 10 ml of 2-methylbutene-1 was passed for 1 hr, discarded, then 125.2 ml of 2-methylbutene-1 passed for 12 hr. The catalyzate ( $n^{20}_D$  1.3856;  $d^{20}_4$  0.6565; bromine number 228.0; 100% of unsaturated compounds), in amount 70 ml, was fractionally distilled (Table 2, Fig. 2, curve 1). Fraction I was 2-methylbutene-1 [ $\Delta\nu$ ,  $cm^{-1}$ : 396 (2w), 773 (9), 1082 (3), 1654 (10), etc.], containing traces of 2-methylbutene-2 [ $\Delta\nu$ ,  $cm^{-1}$ : 1682 (2)]. Fractions II and IV mainly consisted of 2-methylbutene-2 [ $\Delta\nu$ ,  $cm^{-1}$ : 527 (4), 769 (10), 1389 (5), 1682 (10), etc.], while fraction III was practically pure [ $\Delta\nu$ ,  $cm^{-1}$ : 527 (3), 769 (10), 1389 (4), 1682 (10) etc.]. In fractions II and III traces of 2-methylbutene-1 occurred, indicated by the presence of the frequency 1654  $cm^{-1}$  in the spectra of these fractions. Data in the literature for 2-methylbutene-2 [9]: b. p. 38.53°;  $n^{20}_D$  1.3874;  $d^{20}_4$  0.6623. Thus, 2-methylbutene-1 isomerized into 2-methylbutene-2 to the extent of ~70% by a double bond shift.

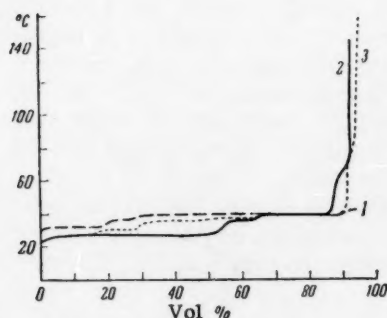


Fig. 1. Distillation curves of the catalyzates in the experiments: 1) experiment 1 (2-methylbutene-1); 2) experiment 2 (2-methylbutene-1 +  $H_2$ ); 3) experiment 3 (2-methylbutene-1 + CO +  $H_2$ ).

### 2-Methylbutene-1 in a current of $H_2$ . Experiment 2 (Table 1)

was carried out with the initial vapor-gas mixture, in which ratio of 2-methylbutene-1:  $H_2$  was 1: 0.94. 87.1 ml of 2-methylbutene-1 and 16.9 liters (NTP) of  $H_2$  were passed. This returned 73.8 ml of liquid catalyzate and 7.9 liters (NTP) of gas. Overall composition of efficient gases and catalyzate degasification gases was (in vol. %) 88.0%  $H_2$ ; 9.0%  $CH_4$ ; 2.1%  $C_2H_6$ ; 0.4%  $C_3H_8$ ; 0.1%  $C_4H_{10}$ ; 0.24%  $C_4H_8$ ; 0.4%  $i-C_5H_{12}$ . Ratio of  $C_1$ :  $C_2$ :  $C_3$ :  $C_4$  was 1: 0.23: 0.4: 0.038. Yield of  $C_1$ - $C_4$  fraction on olefin passed was 5.5%. Sixty-two ml of catalyzate was fractionally distilled (Table 3, Fig. 1, curve 2). Fractions I and II, boiling in the range 24-27.8° and united together, contained 92% 2-methylbutane [ $\Delta\nu$ ,  $cm^{-1}$ : 463 (4), 765 (10), 798 (9), 1037 (3), etc.] and 8% 2-methylbutene-1 [ $\Delta\nu$ ,  $cm^{-1}$ : 1654 (2)]. Data in the literature for 2-methylbutane [9]: b. p. 27-85°;  $d^{20}_4$  0.6197;  $n^{20}_D$  1.3537. Fraction III contained 83% 2-methylbutane [ $\Delta\nu$ ,  $cm^{-1}$ : 765 (10), 798 (8), 1147 (2), etc.] and 17% 2-methylbutene-1 [ $\Delta\nu$ ,  $cm^{-1}$ : 1082 (0), 1418 (0), 1654 (5), etc.]. Fraction IV contained 67% 2-methylbutene-2 [ $\Delta\nu$ ,  $cm^{-1}$ : 527 (4), 769 (10), 1340 (5), 1683 (10), etc.] with a slight impurity of 2-methylbutene-1 [ $\Delta\nu$ ,  $cm^{-1}$ : 1435 (0), 1654 (1)] and 33% of 2-methylbutane [ $\Delta\nu$ ,  $cm^{-1}$ : 798 (4), 1147 (0)]. Fraction V was a mixture of 94% 2-methylbutene-2 [ $\Delta\nu$ ,  $cm^{-1}$ : 527 (3), 769 (10), 1389 (4), 1682 (10), etc.] and 6% 2-methylbutane with traces of 2-methylbutene-1 [ $\Delta\nu$ ,  $cm^{-1}$ : 1654 (0)]. Fraction VI was a mixture of 3-methylalkanes [ $\Delta\nu$ ,  $cm^{-1}$ : 446 (4), 817 (4), 1038 (2), 1147 (1w), etc.] and the corresponding alkenes, and also of 2-methylbutene-2 [ $\Delta\nu$ ,  $cm^{-1}$ : 527 (2), 769 (5), 1340 (2), 1682 (10), etc.].

Thus, 2-methylbutene-1 in presence of hydrogen was hydrogenated to isopentane to the extent of ~47% isomerized to 2-methylbutene-2 to the extent of ~26%, underwent hydrocracking to the extent of 6%, and was converted into higher homologs to the extent of ~7%.

TABLE 1. Experimental Conditions and Results Obtained

Number of expt.	of con-tact	Initial olefin	Expt. duration, hours	Initial gas	Flow rate, hour <sup>-1</sup>			Gas conversion, %	Liquid catalyze yield, vol. % on initial olefin
					olefin	CO	H <sub>2</sub>		
1	1	2-Methylbutene-1	12,0	—	0,35	—	—	—	77,0
2	1	"	8,0	H <sub>2</sub>	0,36	—	70,5	53,2	84,6
3	1	"	12,0	CO+H <sub>2</sub>	0,36	7,0	54,2	47,0	89,5
4	2	3,3-Dimethylbutene-1	8,0	—	0,2	—	—	—	80,2
5	2	"	8,0	H <sub>2</sub>	0,19	—	45,0	51,0	91,0
6	2	"	8,0	CO+H <sub>2</sub>	0,19	4,3	38,2	53,8	92,8

TABLE 2. Catalyze Fractions in Experiment 1 (2-methylbutene-1 without gas-carrier)

Fraction number	Boiling range of fraction, °C	Yield of fraction, vol. %	Fraction properties		Hydrocarbon
			$d_4^{20}$	$n_D^{20}$	
I	30,5—31,5	20,1	0,6501	1,3782	2-Methylbutene-1
II	32,5—37,2	8,5	0,6533	1,3839	2-Methylbutene-2
III	37,8—38,4	61,5	0,6619	1,3874	
IV	38,4—42,5	5,7	0,6590	1,3930	
	Losses	4,2			

2-Methylbutene-1 in a current of a gaseous mixture of CO and H<sub>2</sub>. Experiment 3 (Table 1) was carried out with a triple mixture of 2-methylbutene-1 - CO - H<sub>2</sub>. The initial vapor-gas mixture had the composition: 55.4% i-C<sub>5</sub>H<sub>10</sub>, 5.1% CO and 39.5% H<sub>2</sub>. 130 ml of 2-methylbutene-1, 19.5 liters (NTP) of H<sub>2</sub>, and 2.52 liters (NTP) of CO were passed. This returned 116.8 ml of liquid catalyze and 11.7 liters (NTP) of gas of composition: 83.1% H<sub>2</sub>; 0.6% CO; 7.86% CH<sub>4</sub>; 2.55% C<sub>2</sub>H<sub>6</sub>; 0.21% C<sub>2</sub>H<sub>4</sub>; 1.1% C<sub>3</sub>H<sub>6</sub>; 0.7% C<sub>3</sub>H<sub>8</sub>; 1.4% i-C<sub>4</sub>H<sub>10</sub>; 0.5% C<sub>4</sub>H<sub>8</sub> and 1.5% i-C<sub>4</sub>H<sub>8</sub>. Ratio of C<sub>1</sub>:C<sub>2</sub>:C<sub>3</sub>:C<sub>4</sub> in the gas was 1:0.34:0.25:0.46. Yield of hydrocarbons C<sub>1</sub>-C<sub>4</sub> in relation to olefin passed amounted to 8.5%. One-hundred ml of catalyze was fractionally distilled (Table 4, Fig. 1, curve 3). Fraction I consisted of 30% 2-methylbutene-1 [ $\Delta\nu$ , cm<sup>-1</sup>: 1082 (2), 1654 (9)] and 70% 2-methylbutane [ $\Delta\nu$ , cm<sup>-1</sup>: 463 (3), 798 (6), 1037 (3), 1147 (1), etc.]. Fraction II contained 74% 2-methylbutene-1 [ $\Delta\nu$ , cm<sup>-1</sup>: 396 (0), 773 (9), 1082 (3), 1654 (10), etc.] and 26% 2-methylbutane [ $\Delta\nu$ , cm<sup>-1</sup>: 463 (0), 798 (1)]. Traces of 2-methylbutene-2 were also observed [ $\Delta\nu$ , cm<sup>-1</sup>: 1682 (1)]. Fractions III and IV consisted mainly of 2-methylbutene-2 [ $\Delta\nu$ , cm<sup>-1</sup>: 527 (5), 769 (10), 1340 (6), 1682 (10), etc.] with a slight impurity of 2-methylbutane, and 2-methylbutene-1 [ $\Delta\nu$ , cm<sup>-1</sup>: 1654 (1)]. Fraction V was mainly a mixture of 3-methylalkanes and the corresponding alkenes [ $\Delta\nu$ , cm<sup>-1</sup>: 446 (2), 817 (3), 1038 (2), 1147 (0 w), 1305 (2), etc.] with an impurity of 2-methylbutene-2 [ $\Delta\nu$ , cm<sup>-1</sup>: 527 (1), 769 (4), 1340 (1), 1682 (8), etc.].

Thus, 2-methylbutene-1, in the presence of CO and H<sub>2</sub> was hydrogenated to isopentane to the extent of ~15%, isomerized to 2-methylbutene-2 to the extent of ~54%, converted to higher homologs to the extent of ~5.5%, and underwent hydrocracking to a certain degree. It is noticed that the presence of CO in the initial vapor-gas mixture to a large extent inhibits hydrogenation not only of initial 2-methylbutene-1, but also of its isomerization product, 2-methylbutene-2.

#### Experiments with 3,3-Dimethylbutene-1

3,3-Dimethylbutene-1. In experiment 4 (Table 1) the behavior of 3,3-dimethylbutene-1 alone was investigated. Before the experiment, the catalyst after regeneration was treated with a current of nitrogen to remove hydrogen from the system. Hydrogen adsorbed on the catalyst was accepted by the initial hydrocarbon; the first 5 ml of catalyze were discarded. 47.8 ml of 3,3-dimethylbutene-1 was passed over the catalyst, returning 38.4 ml of

catalyzate and 0.1 liter of gas (nitrogen). The catalyzate ( $n_D^{20}$  1.3788;  $d_4^{20}$  0.6551, bromine number 190.5; 100% unsaturated compounds) contained 86.5% unchanged 3,3-dimethylbutene-1 and 9.4% higher-boiling residue (Table 5, Fig. 2, curve 1).

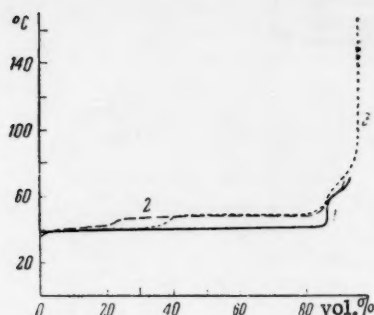


Fig. 2. Distillation curves of catalyzates in the experiments: 1) experiment 4 (3,3-dimethylbutene-1); 2) experiment 5 (3,3-dimethylbutene-1 +  $H_2$ ); 3) experiment 6 (3,3-dimethylbutene-1 +  $CO + H_2$ ).

total gaseous mixture was 43.0 hour<sup>-1</sup>. This returned 42.6 ml of catalyzate and 4.75 liters (NTP) of a gas of composition 0.8%  $CO$ , 85.0%  $H_2$ , 13.6%  $CH_4$ , 0.7%  $C_2H_6$ . Hydrogen reacted to the extent of 56.0%, carbon monoxide 97%. Forty ml of catalyzate was fractionally distilled (Table 7, Fig. 2, curve 3). Fraction I consisted of ~90% unchanged 3,3-dimethylbutene-1 and 10% 2,2-dimethylbutane. Fraction II contained 95% 2,2-dimethylbutane and 5% initial 3,3-dimethylbutene-1. Hydrocarbons boiling higher than neohexane constituted 11.5% of the catalyzate volume, i.e., not much more than in the catalyzate obtained from the mixture of 3,3-dimethylbutene-1 and  $H_2$  in absence of  $CO$  (in experiment 5). From an examination of the data given it is seen that both 2-methylbutene-1 and 3,3-dimethylbutene-1 are practically unreactive in hydrocondensation with  $CO$  and in hydropolymerization under the action of  $CO$  and  $H_2$ . 2-Methylbutene-1 mixed with  $H_2$  in presence of ~5%  $CO$  is ~15% hydrogenated to isopentane, ~54% isomerized to 2-methylbutene-2, and 5.5% converted to higher hydrocarbons. Mixed with  $H_2$ , 2-methylbutene-1 was ~47% hydrogenated to isopentane, ~26% isomerized with shifting of the double bond, ~7% converted into higher hydrocarbons, and underwent hydrocracking to the extent of 6%. In absence of  $CO$  and  $H_2$ , 2-methylbutene-1 was ~70% isomerized to 2-methylbutene-2. According to the data obtained in this work and previously [2, 3], it can be considered that on the surface of the Co-clay catalyst a reversible reaction (2) occurs. Under hydropolymerization conditions reaction (2) is displaced to the right practically completely (content of form 1 was 5-10%). Since  $\beta$ -olefins are hydropolymerized by the action of  $CO$  and  $H_2$ , being first isomerized to  $\alpha$ -olefins [1, 6], it can be

**3,3-Dimethylbutene-1 in a current of  $H_2$ .** In experiment 5 (Table 1) the behavior of 3,3-dimethylbutene-1 in a current of  $H_2$  was studied. The composition of the initial vapor-gas mixture was 41% olefin and 59%  $H_2$ . 46.8 ml of hydrocarbon and 10.85 liters (NTP) of hydrogen were passed. This returned 42.5 ml of catalyzate and 5.2 liters (NTP) of a gas of composition 93.0%  $H_2$ , 6.2%  $CH_4$ , 0.6%  $C_2H_6$ , 0.2%  $C_2H_4$ . Forty ml of catalyzate was fractionally distilled (Table 6, Fig. 2, curve 2). Fraction I was a mixture of 84% initial 3,3-dimethylbutene-1 and 16% 2,2-dimethylbutane (neohexane); fraction (II) - neohexane with an impurity of ~5% of initial 3,3-dimethylbutene-1; fraction III - higher-boiling hydrocarbons. Data in the literature for neohexane [9]: b. p. 49.74°;  $n_D^{20}$  1.3688;  $d_4^{20}$  0.6492. The presence in the catalyzate of small amounts of hydrocarbons boiling below 3,3-dimethylbutene-1, and also of methane in the effluent gas (up to 4% on olefin passed) indicates the occurrence of a small amount of destructive hydrogenation.

**3,3-Dimethylbutene-1 in a current of a gaseous mixture of  $CO$  and  $H_2$ .** In experiment 6 (Table 1) the initial vapor-gas mixture had the composition 43.6% 3,3-dimethylbutene-1, 4.4%  $CO$ , and 52%  $H_2$ . Ratio of  $H_2$ : $CO$  in the initial gas was 8.9. 46.0 ml of olefin, 9.15 liters (NTP) of  $H_2$ , and 1.03 liters (NTP) of  $CO$  were passed. Flow rate of the

TABLE 3. Catalyzate Fractions in Experiment 2 (2-methylbutene-1 in presence of hydrogen)

Fraction number	Boiling range of fraction, °C	Yield of fraction, vol. %	Fraction properties				Hydrocarbon
			$d_4^{20}$	$n_D^{20}$	bromine number	unsaturated substances, %	
I	24.0—27.0	9.0	—	1.3530	17.7	7.8	2-Methylbutane +
II	27.0—27.8	35.0	0.6201	1.3556			
III	27.8—30.0	10.7	0.6222	1.3588	39.9	17.4	+ 2-Methylbutene-1
IV	31.2—37.2	12.0	0.6437	1.3758	153.2	67.0	2-Methylbutane +
V	37.8—39.0	23.3	0.6619	1.3868	215.5	94.0	+ 2-Methylbutene-2
VI	40—145	7.6	0.6777	1.3840	22.6	—	3-Methylalkanes
Losses	—	2.4	—	—	—	—	and alkenes
Initial catalyzate	—	100	0.6343	1.3680	93.8	41.0	—

TABLE 4. Catalyzate Fractions of Experiment 3 (2-methylbutene-1 in presence of CO and H<sub>2</sub>)

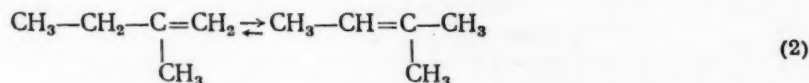
Fraction number	Boiling range of fraction, °C	Yield of fraction, vol. %	Fraction properties				Hydrocarbon
			d <sub>4</sub> <sup>20</sup>	n <sub>D</sub> <sup>20</sup>	bromine number	unsaturated substances, %	
I	24,5—29,5	17,0	0,6251	1,3604	67,8	29,6	2-Methylbutane + 2-Methylbutene-1
II	30—32,0	11,4	0,6407	1,3725	169,5	74,2	
III	33,2—38,0	20,0	0,6536	1,3832	213,0	93,0	2-Methylbutene-2
IV	38,0—39,2	42,2	0,6618	1,3870	—	—	
V	40—162	6,0	0,6901	1,3958	51,2	—	3-Methylalkanes and alkenes
	Losses	3,4	—	—	—	—	
	Initial catalyzate	100	0,6506	1,3810	179,0	78,4	

TABLE 5. Catalyzate Fractions in Experiment 4 (3,3-dimethylbutene-1 in absence of gas-carrier)

Fraction No.	Boiling range of fraction, °C	Yield of fraction, vol. %	Properties of fraction		Hydrocarbon
			d <sub>4</sub> <sup>20</sup>	n <sub>D</sub> <sup>20</sup>	
I	39,5—41	86,5	0,6528	1,3765	3,3-Dimethylbutene-1
II	50—71	9,4	—	1,3950	
	Losses	4,1	—	—	

TABLE 6. Catalyzate Fractions in Experiment 5 (3,3-dimethylbutene-1 in a current of H<sub>2</sub>)

Frac. No.	Boiling range of fraction, °C	Yield of fraction, vol. %	Properties of fraction				Hydrocarbon
			d <sub>4</sub> <sup>20</sup>	n <sub>D</sub> <sup>20</sup>	bromine number	unsaturated compounds	
1	37,5—48,0	24,0	0,6498	1,3730	129,7	84,0	3,3-Dimethylbutene-1 + 2,2-dimethylbutane
2	48,5—49,0	60,0	0,6494	1,3690	10,4	5,4	
3	50—74	8,5	0,6624	1,3790	38,45	20,2	
	Losses	7,5	—	—	—	—	
	Initial catalyzate	100	0,6499	1,3715	40,5	21,2	



proposed that the rate of the reverse reaction (2) is considerable lower than the hydropolymerization rate, which probably explains to a certain extent the low reactivity of 2-methylbutene-1 in the reactions indicated. The possibility is not excluded that the 2-methylbutene-1 molecule is of itself of low reactivity in hydropolymerization in absence of isobutylene and n-pentene molecules. 3,3-Dimethylbutene-1 was ~43% hydrogenated in presence of CO and H<sub>2</sub>, and mixed with H<sub>2</sub>, about 57%. In all the catalyzates obtained in experiments with 3,3-dimethylbutene-1, a fraction occurred with b. p. 50–74°, amounting to 7–9,5%. Higher-boiling hydrocarbons with b. p. 74–168° occurred



TABLE 7. Catalyzate Fractions in Experiment 6 (3,3-dimethylbutene-1 in a current of gaseous mixture of CO and H<sub>2</sub>)

Fraction No.	Boiling range of fraction, °C	Yield of fraction, vol. %	Properties of fraction				Hydrocarbon
			d <sup>20</sup> <sub>4</sub>	n <sup>20</sup> <sub>D</sub>	bromine number	unsaturated compounds	
I	37-48,0	40,0	0,6496	1,3750	172,0	90,0	3,3-Dimethylbutene-1 + + 2,2-di-methylbutane 2,2-Dimethylbutane
II	49-50	45,0	0,6492	1,3692	10,1	5,3	
III	50,5-74	6,5	0,6691	1,3835	53,7	37,5	
IV	74-168	5,0					
	Losses	3,5	—	—	—	—	
	Initial catalyst	100	0,6508	1,3738	80,6	42,4	

in the catalyzate obtained from the triple mixture 1-C<sub>6</sub>H<sub>12</sub> - CO - H<sub>2</sub>. This fraction, which can be regarded as the hydrocondensation product of 3,3-dimethylbutene-1 with CO, amounted in all to 5% of catalyzate volume. The low activity of 3,3-dimethylbutene-1 in hydropolymerization and hydrocondensation reactions with CO and H<sub>2</sub> is evidently bound up with the steric difficulty in adsorbing the olefin on the catalyst surface.

#### SUMMARY

1. The conversions of 2-methylbutene-1 and 3,3-dimethylbutene-1 under hydrocondensation catalytic conditions were studied.
2. Mixed with H<sub>2</sub> in presence of ~5% CO, 2-methylbutene-1 was semi- isomerized to 2-methylbutene-2 with a double bond shift, hydrogenated in isopentane, and only reacted to a slight extent to form higher hydrocarbons. 3,3-Dimethylbutene-1 under similar conditions was mainly hydrogenated to neohexane and was only partially converted to higher hydrocarbons.
3. In absence of CO and under the action of H<sub>2</sub>, the same reactions occurred for both hydrocarbons, hydrogenation prevailing over isomerization in addition, hydrocracking of the initial olefins occurred to a slight extent.
4. In absence of CO and H<sub>2</sub>, 2-methylbutene-1, unlike pentene-1, underwent isomerization with transfer of the double bond to the  $\beta$ -position.

#### LITERATURE CITED

1. Ya. T. Éidus and M. B. Ordyan, *Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk* **1957**, 1410; **1958**, 243.
2. Ya. T. Éidus and N. I. Ershov, *Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk* **1959**, 1312.
3. Ya. T. Éidus, K. V. Puzitskii, and A. P. Meshcheryakov, *Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk* **1954**, 149.
4. Ya. T. Éidus, N. I. Ershov, and E. M. Terent'eva, *Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk* **1954**, 882.
5. N. I. Ershov, Ya. T. Éidus, and V. R. Erokhina, *Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk* **1960**, 366.
6. Ya. T. Éidus and R. I. Izmailov, *Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk* **1956**, 467, 457, 723, 869.
7. Ya. T. Éidus, K. V. Puzitskii, and M. I. Batuev, *Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk* **1952**, 978.
8. Ya. T. Éidus and B. K. Nefedov, *Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk* **1960**, 349.
9. R. D. Obolentsev, *Physical Constants of Hydrocarbons of Liquid Fuels and Oils* [in Russian] Gostoptekhlizdat, **1953**.
10. *Syntheses of Organic Compounds* [in Russian] Collection 1, IL. Moscow, **1949**, p. 340.
11. I. Guben, *Methods of Organic Chemistry* [in Russian] Vol. 2, No. 1, Goskhimizdat, Moscow-Leningrad, **1941**, p. 332.
12. P. L. Cramer and A. L. Glasebrook, *J. Amer. Chem. Soc.* **61**, 230 (1939); E. A. Kelso, G. Wash, J. T. Horeczy, B. Shive, and W. A. Felsing, *J. Amer. Chem. Soc.* **63**, 2273 (1941).

13. Ya. T. Éidus, N. D. Zelinskii, and K. V. Puzitskii, *Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk* **1949**, 110.
14. G. S. Landsberg, P. A. Bazhulin, and M. M. Sushchinskii, *Basic Parameters of Raman Spectra of Hydrocarbons*, *Izvest. Akad. Nauk SSSR*, (Moscow, 1956).

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

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## A STUDY OF THE HYDROBROMINOLYSIS\* OF GLYCINE ESTERS

K. T. Poroshin, V. G. Debabov, and Vyach. I. Maksimov

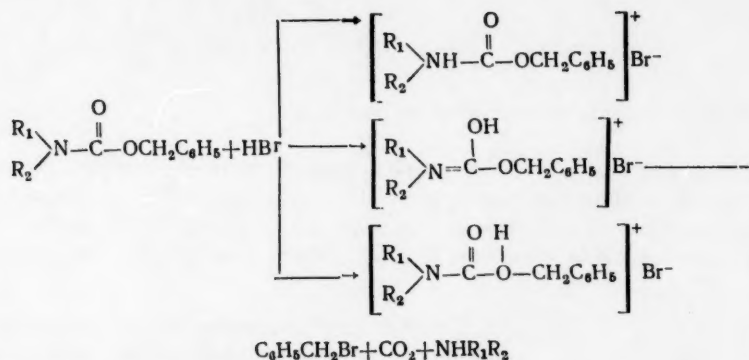
N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR

Translated from *Izvestiya Akademii Nauk, Otdeleniye Khimicheskikh Nauk*.

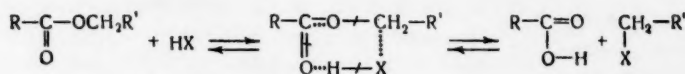
No. 6, pp. 1134-1137, June, 1961

Original article submitted June 24, 1960

In view of the exceptionally wide use of hydrogen bromide solution in glacial acetic acid in synthesis of peptides it is of interest to study in more detail the action of this reagent on esters, and also in passing to elucidate the problem of the action of hydrogen bromide in acetic acid on the peptide linkage. According to Ben-Ishai and Berger [1], the reaction of esters with HBr in acetic acid is neither hydrolysis nor reduction, but is a case of acidolysis and must proceed, in their opinion, by one of three routes.



Here the action is observed of  $\text{HBr}/\text{CH}_3\text{COOH}$  only on the carbobenzoxy group, although it is known that this reagent acts on other esters. In addition, this mechanism does not explain the effect of the solvent on the process, since it is known that the addition of water leads to retardation of the reaction and even to its course via a hydrolytic route. It appeared to us, in the light of the views developed by Syrkin [2] on the role of intermediate complexes in chemical reactions, that acidolysis in this instance proceeds according to the following scheme (here the symbols are those used by Syrkin).



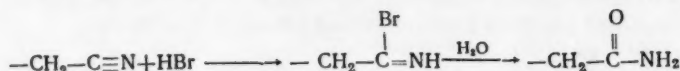
where X=Cl; Br; I

According to this mechanism for formation of an intermediate complex the presence is necessary of an undissociated HBr molecule, which condition is fully achieved in such solvents as glacial acetic acid, nitromethane, and absolute alcohol. As already noted, HBr in glacial  $\text{CH}_3\text{COOH}$  acts on other esters, although it is of value in preparation of benzyl esters and in protecting the amino group in several cases of compounds of the urethane type

$\left[ \begin{array}{c} \text{(R-O-C-N<)} \\ \parallel \\ \text{O} \end{array} \right]$ . The latter can also be regarded as an ester. From the literature it is known that benzyl esters

\* We define "hydrobrominolysis" as the action of splitting an ester with HBr to the free acid and alkyl bromide. This term is not generally acknowledged.

undergo hydrobrominolysis most readily, *p*-nitrobenzyl and methyl esters with much greater difficulty. However, this reaction has scarcely been studied systematically under standard conditions. The Polish authors [3] who have attempted a study of the reaction clearly came to an incorrect conclusion on this subject, namely, that the alcoholic residue has no effect on acidolysis rate. A few esters have been studied by these authors: ( $-\text{OCH}_3$ ;  $-\text{OC}_2\text{H}_5$ ;  $-\text{OCH}_2\text{CN}$ ). It was natural that it was difficult to observe a substantial difference in the behavior of the methyl and the ethyl ester, but it is rather strange that the authors did not point out that the cyanomethyl ester behaves differently in this reaction to the others, inasmuch as, as shown by Goodman et al. [4], it reacts with HBr according to the following scheme:



The aim of the present work was the investigation of the effect of the alcoholic residue of glycine esters on hydrobrominolysis rate. We studied the hydrobrominolysis of the following glycine esters: benzyl, cyclohexyl, *p*-nitrobenzyl, and methyl, prepared mainly by methods described in the literature (except the cyclohexyl). We evolved a method of controlling the course of acidolysis according to the glycine formed as a result of the reaction, the glycine being quantitatively determined by colorimetry of chromatograms fully developed with ninhydrin.

The result of the work is shown in the diagram of Fig. 1, where it is clearly seen that with increase in nucleophilic properties of the alkyl group in the series



the rate of splitting off these groups in hydrobrominolysis increases.

From Fig. 1 it is seen that after 3 hr the benzyl and cyclohexyl esters were completely hydrobrominolized. It is interesting to note that the maximum extinction, shown along the *y* axis, in the case of these esters is identical, and coincides with the extinction of a solution of glycine in glacial acetic acid of the same molarity. The latter fact indicates that on conducting the experiment at  $56 \pm 0.2^\circ$  hydrobrominolysis is not complicated by any side reactions.

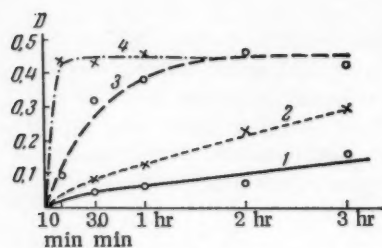


Fig. 1. Relation between rate of hydrobrominolysis of glycine esters and nature of alcoholic residue: 1) methyl ester; 2) nitrobenzyl ester; 3) cyclohexyl ester; 4) benzyl ester. Time is plotted along the *x* axis; along the *y* axis - amount of glycine, expressed in optical density units (*D*).

white powder with *m. p.* 136-138°. Found: C 49.94, 50.10; H 8.26, 8.22%.  $\text{C}_8\text{H}_{16}\text{NO}_2\text{Cl}$ . Calculated: C 49.7; H 8.3%. After two reprecipitations from methyl alcohol by ether, the substance melted at 145° and contained no glycine impurity on the chromatograms developed with ninhydrin.

In the table are given the constants of the glycine esters investigated; melting points were not checked; chromatography was carried out in the system butanol; water; acetic acid 4:5:1; "Leningrad" paper, type "B," lengthwise.

In a series of preliminary experiments we observed that on carrying out the reaction at 80° both glycine esters and glycine itself undergo some conversion with formation of ninhydrin-negative substances. On boiling 0.001 M of glycine solution in glacial  $\text{CH}_3\text{COOH}$  with 40% HBr in a sealed ampoule at 80° for 5 hr, the original glycine extinction falls by one third.

#### EXPERIMENTAL

Hydrochloride of the cyclohexyl ester of glycine. In a three-necked flask with stirrer, reflux condenser, and dropping funnel was suspended 5 g of glycine in 100 ml of cyclohexanol. Over a period of 15 minutes 8 ml of thionyl chloride was added to the suspension, and the solution then boiled for 3-4 hr. The completely transparent solution was washed with water three times to extract the hydrochloride of the cyclohexyl ester of glycine, and the cyclohexanol layer discarded. The aqueous layer was brought to pH 10 with solid potash and extracted with ether. The ethereal extracts were dried over  $\text{Na}_2\text{SO}_4$ . A current of hydrochloride was bubbled into the dry ester, the hydrochloride of the cyclohexyl ester (3.6 g) precipitating as a



Acidolysis of esters. To maintain a constant HBr concentration during the reaction, acidolysis was carried out in sealed ampoules. All reactions were carried out at  $t = 56 \pm 0.2^\circ$  (vapor of boiling acetone). In each case 0.001 M amount of the substance was used in the reaction, this amount being dissolved in 2 ml of glacial acetic acid containing 40% HBr (by weight). After dissolving the ester, the solution was poured into five ampoules, the ampoules sealed and immersed in the vapor of boiling acetone. Samples were withdrawn after 10 and 30 minutes, 1, 2, and 3 hr. After removal from the acetone vapor, the samples were frozen in a mixture of dry ice and acetone. Using a pipette designed for quantitative application, four spots were obtained from each sample on a circular chromatogram of diameter 13 cm.

#### Constants of Glycine Esters Investigated

Glycine esters (hydrochlorides)	$R_f$	M. p., $^\circ\text{C}$	Reference in lit.
Cyclohexyl	0.70	145	[5]
Benzyl	0.63	130	
Methyl	0.36	173-175	
p-Nitrobenzyl (hydrobromide)	0.58	192-198	[6]

the solution was poured into five ampoules, the ampoules sealed and immersed in the vapor of boiling acetone. Samples were withdrawn after 10 and 30 minutes, 1, 2, and 3 hr. After removal from the acetone vapor, the samples were frozen in a mixture of dry ice and acetone. Using a pipette designed for quantitative application, four spots were obtained from each sample on a circular chromatogram of diameter 13 cm.

**Chromatography and colorimetry.** Chromatography was carried out in the system butanol: water: acetic acid 4:5:1, "Leningrad" "B" paper. Duration of chromatograms, 2 hr. Chromatograms were air-dried and developed with 0.5% ninhydrin solution in 95% aqueous acetone, maintaining them at room temperature for 18-20 hr. Glycine spots were eluted with 5 ml of 75% ethyl alcohol containing 70 mg of  $\text{CuSO}_4$  per 100 ml of solution. Elution was continued for 2.5 hr; the test tubes, tightly stoppered were then agitated on a mechanical shaker. Colorimetry was carried out in an FEK-M-50 instrument in cells with  $l = 10$  mm and at  $\lambda = 570$  nm (green filter). Each point on graph 1 is the arithmetic mean of four readings. Maximum deviation from the mean value amounted to  $\sim 10\%$ , average deviation 4%. Reproducibility of experiments, i.e., mean value for the same point in parallel experiments, was low and amount to approximately 10-15%, this, however, did not prevent in any way conclusions being drawn regarding the relative rate of hydrobrominolysis of the esters under investigation.

grams, 2 hr. Chromatograms were air-dried and developed with 0.5% ninhydrin solution in 95% aqueous acetone, maintaining them at room temperature for 18-20 hr. Glycine spots were eluted with 5 ml of 75% ethyl alcohol containing 70 mg of  $\text{CuSO}_4$  per 100 ml of solution. Elution was continued for 2.5 hr; the test tubes, tightly stoppered were then agitated on a mechanical shaker. Colorimetry was carried out in an FEK-M-50 instrument in cells with  $l = 10$  mm and at  $\lambda = 570$  nm (green filter). Each point on graph 1 is the arithmetic mean of four readings. Maximum deviation from the mean value amounted to  $\sim 10\%$ , average deviation 4%. Reproducibility of experiments, i.e., mean value for the same point in parallel experiments, was low and amount to approximately 10-15%, this, however, did not prevent in any way conclusions being drawn regarding the relative rate of hydrobrominolysis of the esters under investigation.

The authors thank G. V. Nikiforova for performing part of the experimental work.

#### SUMMARY

1. A method is presented for determining hydrobrominolysis rate based on amount of glycine formed, employing chromatography of the reaction mixture with subsequent colorimetry.
2. With increase in nucleophilic properties of the alkyl residue, glycine esters hydrobrominolysis rate increases.

#### LITERATURE CITED

1. Ben-Ishai and A. Berger, J. Organ. Chem. **17**, 1564 (1952).
2. Ya. K. Syrkin, Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk **1959**, 239.
3. E. Taschner, G. Kupryszewski, and L. Bogdan, Roczn. chem. **32**, N 5, 107 (1958).
4. M. Goodman and K. G. Stueben, J. Amer. Chem. Soc. **81**, 3980 (1959).
5. H. K. Miller and H. Waelsch, J. Amer. Chem. Soc. **74**, 1092 (1952).
6. H. Schwarz and K. Arakawa, J. Amer. Chem. Soc. **81**, 5691 (1959).

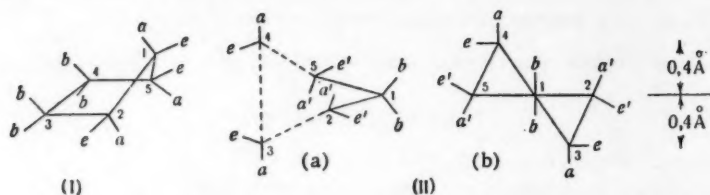
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# OPTICAL INVESTIGATION OF THE CONFORMATIONS OF CYCLOPENTANONE AND $\alpha$ -CHLOROCYCLOPENTANONE

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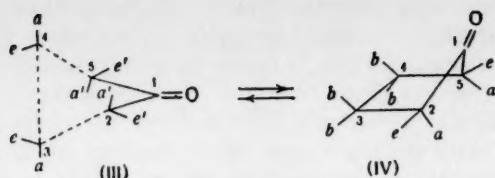
Over the last 15-20 years the stereochemistry of cyclopentane has been the subject of many investigations, varied in the methods employed. It can now be considered established that the cyclopentane ring is nonplanar [1, 13]. If the ring had a planar structure it would be energetically strained, not because of the strain of the tetrahedral direction of the bonds (the angle in a regular pentagon is close to that of a tetrahedron and is equal to  $108^\circ$ ), but because of the mutual repulsion of the hydrogen atoms of the methylene groups; thus, it is not realized in actual practice. Even the withdrawal of one of the carbon atoms from the plane of the other four relieves this strain. This "envelope" form (I) (symmetry  $S$ ) was at first ascribed to the nonplanar structure of cyclopentane with the additional assumption of pseudorotation of the ring, expressed as an alternative departure from planarity of one carbon atom with respect to the other. But as well as this form, certain experimental and calculated data has rendered necessary the idea that a nonplanar structure for cyclopentane is also possible, with two carbon atoms withdrawn from the plane of the remaining three atoms [4, 9, 13] — giving a half-chair form (II) (symmetry  $C_2$ ). (In IIa the dotted lines represent the bonds lying outside the plane of atoms  $C_1C_2C_5$ ).



For cyclopentanes itself, structures (I) and (II) are practically unseparated by an energy barrier. No factor can be suggested which would definitely enable one of these forms to be considered more stable than the other. Thus they cannot be considered as separate conformations determined in certain physical experiments. Structures (I) and (II) are only some of the most probable nonplanar forms in which cyclopentane could exist and for which (I) and (II) are only the limiting forms. In the work [9] the proposition is made that in (II) it is possible that "better mutual arrangement of hydrogen atoms" occurs (see also [13]). However, the almost complete identity of the proton chemical displacement in cyclopentane and cyclohexane, observed by the proton magnetic resonance method [15], apparently points to the overwhelming predominance of form (I) or of one close to it.

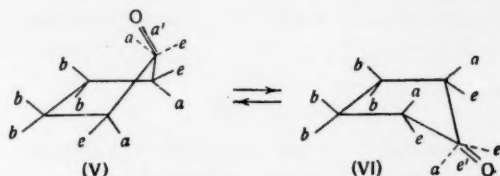
Stabilization of form (I) or (II) of the cyclopentane ring could be expected in polycyclic systems and in various substituted cyclopentanes. It should be noted that only form (I) has been observed experimentally in polycyclic systems so far, for instance — in chloro-, bromo-, and cyano- camphor, in the 4-iodo-5-nitrobenzoate of calciferol and in the iodo-cholesterin ring [16]. In the work [12] an attempt was made to ascertain which substituents in substituted cyclopentanes permit realization of form (I) and which enable that of form (II).

Certain experimental data (microwave spectrum, polarizability) and calculated data [17, 9, 13] indicate a nonplanar character for the cyclopentane ring and in cyclopentanone. In [13] it was proposed that in cyclopentanone this ring is represented mainly by a form with symmetry  $C_2$  (III), occurring to the extent of  $\sim 86\%$  in an equilibrium mixture with (IV), in which the cyclopentane ring has the form with symmetry  $C_s$ .



This proposition was put forward by analogy with the structure of ethylene carbonate, determined by x-ray structural analysis [18], and by calculation of the potential barrier in  $\sim 1$  kcal/M in the conversion (III)  $\rightarrow$  (IV) by the method given in [12]. However, optical data is not in agreement with this proposition.

In the Raman spectrum the carbonyl of cyclopentanone is represented by the frequency doublet 1730, 1747  $\text{cm}^{-1}$  with much greater clarity than in the spectrum of cyclohexanone [19]. As in cyclohexanone [19], we are inclined to relate this doublet to the various conformations of cyclopentanone, differing from each other in the varying position of the carbonyl group in the molecule. In cyclohexanone these varying positions of the carbonyl are quasi-axial ( $a'$ ) and quasiequatorial ( $e'$ ) [19]. In this case, where the carbonyl group is excluded from the plane  $C_1C_2C_5$  into the two quasi-bisectonal positions ( $b'$ ) in (II), the conformations of the molecule would be completely identical (in both cases there would be an interaction between the carbonyl and the C-H bonds in positions  $a, a', e'$ ) and would not guarantee a doublet of C=O frequency. We therefore propose that on substituting the hydrogen atoms of cyclopentane by carbonyl in cyclopentanone stabilization is achieved from the form of the cyclopentane ring with symmetry  $C_5$  (or of a form very close to it) in one conformation (V) with a quasi-axial, in another (VI)—with a quasi-equatorial position of the carbonyl group. Optically, these conformations differ markedly in carbonyl vibrational frequency: the quasi-axial carbonyl is characterized by a lower frequency—1730  $\text{cm}^{-1}$ , the quasi-equatorial—by a higher one—1747  $\text{cm}^{-1}$  (see [19] regarding this).

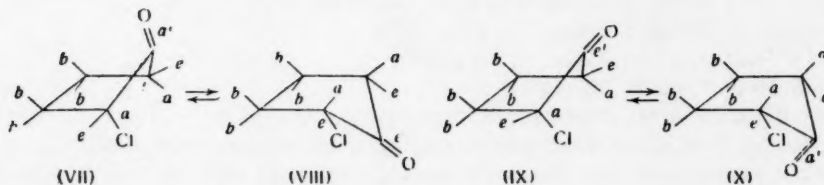


The variable frequency of the ring in the spectrum of cyclopentanone is a double one.

Substitution of an  $\alpha$ -hydrogen atom in cyclopentanone by a chlorine atom could lead to formation of four conformations of  $\alpha$ -chlorocyclopentanone (VII-X), similar to those which we have observed in  $\alpha$ -chlorocyclohexanone [19]. Optically, they are characterized by various C=O and C-Cl vibration frequencies and by varying ring vibration frequencies (see [19] with regard to this)

(VII)trans-1 $a'$ ,2 $a'$   $\rightleftharpoons$  (VIII)trans-1 $e'$ ,2 $e'$  (IX)cis-1 $e'$ ,2 $a'$   $\rightleftharpoons$  (X)cis-1 $a'$ ,2 $e'$

C=O	1751(6)	1772(2)	1760(6)	1746(2)
C-Cl	686(10)	702(3)	680(5)	692(5)
Ring	909(8)	918(6)	892(5)	901(5)



\* This doublet (1726, 1746  $\text{cm}^{-1}$ ) was observed by Piaux in 1933 [20]. But Kohlrausch in 1936 [21] cited only the one frequency, 1733  $\text{cm}^{-1}$ , indicating that it is broad. In 1937 Biquard again observed this doublet (1727, 1744  $\text{cm}^{-1}$ ). Recently this doublet (1728, 1748  $\text{cm}^{-1}$ ) was confirmed in [23]. At the present time, the cyclopentanone C=O frequency doublet is considered a firmly established fact.

In the spectra of both compounds (especially that of the second) a greater number of lines is observed (including double ones) than theoretically needed for one isomer (allowing for degeneration). This fact is convincing confirmation of the idea that the compounds investigated exist in the several conformations and configurations indicated above; on an experimental basis, it directly removes the sole objection to isomerism in cyclopentanone, groundlessly raised in [24]. The explanation of the doublet in the carbonyl region by Fermi resonance [24] is untenable in view of the marked difference in the symmetry of the compounds under investigation and also that of cyclohexanone and its derivatives, investigated by us previously [19], and in view of the absence of it in the corresponding basic frequencies.

#### EXPERIMENTAL

The physical properties of the compounds investigated were: cyclopentanone, b. p. 130° (760 mm);  $n_D^{20}$  1.4365;  $\alpha$ -chlorocyclopentanone, b. p. 65-66° (8 mm);  $n_D^{20}$  1.4737.

Raman spectra determinations were taken on a locally-made ISP-51 spectrograph with a central camera and on a Hilger E612 spectrograph of the excited blue line at 4358 Å on a mercury lamp (for key to intensities see [14].

Cyclopentanone,  $\Delta\nu$ ,  $\text{cm}^{-1}$ : 237 (vbr), 302 (0), 452 (2), 475 (4), 558 (1), 579 (2\*), 591 (2\*), 712 (5), 813 (5), 895 (10db), 955 (3\*), 769 (3\*), 1024 (6), 1154 (4 db), 1196 (1), 1235 (3 db), 1255 (3\*), 1275 (3\*), 1289 (1\*), 1412 (6), 1458 (5\*), 1469 (2\*), 1730 (6\*\*), 1747 (6\*\*), 2881 (10), 2898 (10\*), 2909 (5\*), 2957 (3\*\*), 2972 (10\*\*), 2988 (5\*\*) [the frequency 895 at low intensities was observed as a doublet - 892 (p), 898 (p)].

$\alpha$ -Chlorocyclopentanone,  $\Delta\nu$ ,  $\text{cm}^{-1}$ : 199 (4\*br,db), 216 (4\*br,db), 327 (5\*\*db), 339 (1\*\*), 408 (3br,db), 460 (3br,db), 521 (5), 608 (5br), 680 (5\*s), 686 (10\*s), 692 (5\*s), 702 (3\*s), 806 (3\*\*), 816 (3\*\*), 839 (3\*), 849 (3\*), 876 (1), 892 (6\*s), 901 (5\*s), 909 (8\*\*), 918 (6\*\*), 944 (0), 961 (3 db), 1003 (4\*), 1013 (2\*), 1041 (4\*\*), 1054 (4\*\*), 1114 (3 db), 1145 (0\*), 1162 (4\* db), 1234 (4 db), 1241 (4 db), 1279 (5 db), 1306 (2\*), 1319 (0\*), 1346 (1), 1409 (6), 1439 (2\*), 1455 (6\*), 1470 (2\*), 1746 (2\*s), 1751 (6\*s), 1760 (6\*s), 1772 (2\*s), 2848 (0\*), 2867 (0\*), 2881 (6\*db), 2897 (2\*s), 2904 (6\*s), 2916 (10\*s), 2930 (5\*s), 2968 (2\*s), 2971 (6\*s), 2983 (10\*s), 2997 (3\*s), 3010 (2\*s).

#### SUMMARY

Cyclopentanone exists in two conformations - with a quasi-axial (V) and a quasi-equatorial (VI) position for the carbonyl group.  $\alpha$ -Chlorocyclopentanone exists in four conformations: (VII) trans-1a'-2a  $\rightleftharpoons$  (VIII) trans-1e'2e, (IX) cis-1a'2a  $\rightleftharpoons$  (X) cis-1a'2e.

#### LITERATURE CITED

1. J. Aston, S. Schumann, H. Fink, and P. Daty, J. Amer. Chem. Soc. **63**, 2029 (1941).
2. J. Aston, H. Fink, and S. Schumann, J. Amer. Chem. Soc. **65**, 341 (1943).
3. J. Kilpatrick, K. Pitzer, and R. Spitzer, J. Amer. Chem. Soc. **69**, 2483 (1947).
4. O. Bastiansen, O. Hassel, and L. Lund, Acta chem. scand. **3**, 297 (1949).
5. F. Miller and R. Inskep, J. Chem. Phys. **18**, 1519 (1950).
6. H. Tschamler and R. Voetter, Monatsh. **83**, 302, 835, 1228 (1952).
7. J. S. Barker and R. Stephens, J. Chem. Soc. **1954**, 4550.
8. M. Newman (Ed.), Steric Effects in Organic Chemistry, New York, 1956.
9. C. G. LeFevre and R. J. LeFevre, J. Chem. Soc. **1956**, 3549.
10. B. Curnutte and W. Shaffer, J. Mol. Spectr. **1**, 239 (1957).
11. J. McCullough, J. Chem. Phys. **29**, 966 (1958).
12. K. Pitzer and W. Donath, J. Amer. Chem. Soc. **81**, 3213 (1959).
13. F. Brucher, T. Roberts, S. Barr, and N. N. Pearson, J. Amer. Chem. Soc. **81**, 4915 (1959).
14. M. I. Batuev, A. A. Akhrem, and A. D. Matveeva, Doklady Akad. Nauk SSSR **129**, 1038 (1959).
15. J. Pople, W. Schneider, and H. Bernstein, High-resolution Nuclear Magnetic Resonance, New York, 1959.
16. A. Wiebenga and A. Krom, Recueil trav. chim. **65**, 663 (1946); D. Crowfoot and J. Dunitz, Nature **162**, 608 (1948); C. Carlisle and D. Crowfoot, Proc. Roy. Soc. **A184**, 64 (1945).
17. G. Erlanson, J. Chem. Phys. **22**, 563 (1954).
18. C. Brown, Acta crystallogr. **7**, 92 (1954).
19. M. I. Batuev, A. A. Akhrem, A. V. Kamernitskii, and A. D. Matveeva, Doklady Akad. Nauk SSSR **133**, 1077 (1960).



20. M. Plaux, *Compt. rend.* 197, 1647 (1933).
21. K. Kohlrausch, A. Reitz, and W. Stockmair, *Z. phys. Chem.* B32, 229 (1936).
22. D. Blquard, *Compt. rend.* 204, 1721 (1937).
23. G. Michel and G. Duyckaerts, *Spectrochim. acta* 10, 259 (1958); G. Michel, *Bull. Soc. chim. belges* 68, 643 (1959).
24. G. Allen, P. Ellington, and G. Meakins, *J. Chem. Soc.* 1960, 1909.

---

All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

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## BRIEF COMMUNICATIONS

### SYNTHESIS OF 1-n-BUTYLTHIOBORACYCLOALKANES

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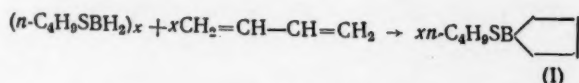
Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*,

No. 6, pp. 1142-1144, June, 1961

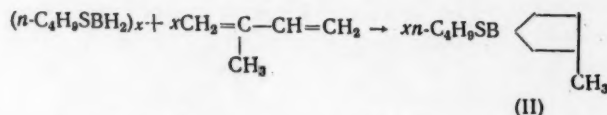
Original article submitted October 22, 1960

Previously we had found that the reaction of diborane with n-butyl mercaptan, taken in a 1:2 ratio, yields a polymer of n-butylthioborane. Further it was established that in ether solution the polymer adds to olefins, forming the n-butyl esters of dialkylthioboronic acids [1, 2]. It proved that the polymer of butylthioborane behaves in a similar manner toward dienic hydrocarbons. Reaction of the dienic hydrocarbon with an ether solution of the polymer at room temperature yields the corresponding 1-n-butylthioboracycloalkane.

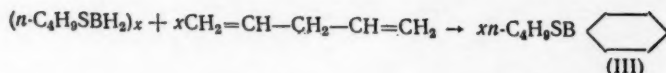
By reacting butadiene with n-butylthioborane we obtained 1-n-butylthioboracyclopentane (I), which proved to be a colorless liquid, oxidizing with exceeding ease in the air.



The structure of the 1-n-butylthioboracyclopentane was established by oxidation with hydrogen peroxide, in which connection 1,4-butanediol was obtained, identified as the dibenzoate. The reaction with isoprene proceeds in a similar manner, resulting in the formation of 3-methyl-1-n-butylthioboracyclopentane (II).



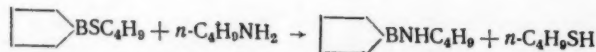
The reaction of 1,4-pentadiene with n-butylthioborane gave 1-n-butylthioboracyclohexane (III).



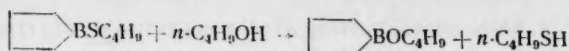
The last two compounds are also characterized by a much greater sensitivity toward oxygen than the dialkylthioboronic esters.

Boron-containing heterocyclic compounds with hydrocarbon substituents on the boron atom were previously obtained from organoboron halides and the corresponding dilithium [3] or dimagnesium [4] derivatives of butane or pentane, and also by the addition of diborane [5], 1,2-diaryldiboranes [6] or the trimethylamine complex of tert-butylborane [7] to dienic hydrocarbons. Transition from the boracyclic compounds synthesized by the enumerated methods to functional derivatives with substituents on the boron atom cannot be accomplished [6]. In contrast, the presence of an exceedingly reactive alkylthio group on the boron in the compounds obtained by us opens up great possibilities of utilizing them for the synthesis of various derivatives of boron-containing heterocycles.

Thus, when 1-n-butylthioboracyclopentane is reacted with n-butylamine it is converted in 74% yield to 1-n-butylaminoboracyclopentane. The reaction of 1-n-butylthioboracyclopentane with n-butyl alcohol goes somewhat less smoothly. Here the yield



of the corresponding butoxyl derivative is only 44%. In this case the substitution reaction is probably accompanied



by a partial cleavage of the ring carbon-boron bond.

## EXPERIMENTAL

In all of the experiments with the dienes we used an ether solution of the *n*-butylthioborane polymer, which was obtained by the passage of 0.108 mole of diborane into a solution of 17.2 g (0.19 mole) of *n*-butyl mercaptan in 100 ml of ether over a period of 5 hr.

**1-*n*-Butylthioboracyclopentane.** Butadiene was passed into an ether solution of the alkylthioborane until the spontaneous heating up of the reaction mixture ceased. The solvent was removed in vacuo, while the residue was subjected to fractional distillation. We obtained: 1) 11.5 g (33%) of 1-*n*-butylthioboracyclopentane with b. p. 45-49° (2 mm);  $d_4^{20}$  0.9326;  $n_D^{20}$  1.5090; found MR 49.91; calculated MR 50.01. Found: C 62.49, 62.80; H 11.35, 11.39; B 7.23, 7.41%.  $\text{C}_8\text{H}_{17}\text{BS}$ . Calculated: C 61.55; H 10.98; B 6.93%; 2) 9.2 g of tetra(*n*-butylthio)diborane with b. p. 98-102° (2 mm).

The oxidation of 1-*n*-butylthioboracyclopentane with hydrogen peroxide in alcoholic caustic solution [8] gave 1,4-butylene glycol, which was isolated in 86% yield as the dibenzoate; m. p. 76-78°. Literature data [9]: 80-81°.

**3-Methyl-1-butylthioboracyclopentane.** Isoprene (21.0 g; 0.3 mole) was added from a dropping funnel to an ether solution of the *n*-butylthioborane polymer, in which connection the reaction mixture warmed up. The residue from the removal of the solvent was subjected to fractional distillation. We obtained: 1) 17.7 g (55%) of 3-methyl-1-butylthioboracyclopentane with b. p. 52-55° (1 mm);  $d_4^{20}$  0.8836;  $n_D^{20}$  1.4822; found MR 54.94; calculated MR 54.66. Found: C 63.43, 63.91; H 11.27, 11.25; B 6.52, 6.44%.  $\text{C}_9\text{H}_{19}\text{BS}$ . Calculated: C 63.53; H 11.26; B 6.36%; 2) 4.4 g of tetra(*n*-butylthio)diborane with b. p. 90-95° (1 mm).

**1-*n*-Butylthioboracyclohexane.** The addition of 21.0 g (0.3 mole) of 1,4-pentadiene to an ether solution of the *n*-butylthioborane polymer was accompanied by the evolution of heat. The ether was distilled from the reaction mixture; the residue was subjected to fractional distillation. We obtained: 1) 19.3 g (60%) of 1-*n*-butylthioboracyclohexane with b. p. 54-58° (1 mm);  $d_4^{20}$  0.8932;  $n_D^{20}$  1.4850; found MR 54.59. Found: C 64.61, 64.67; H 11.44, 11.41; B 6.25, 6.11%.  $\text{C}_9\text{H}_{19}\text{BS}$ . Calculated: C 63.53; H 11.26; B 6.36%; 2) 5.3 g of tetra(*n*-butylthio)diborane with b. p. 92-98° (1 mm).

**1-*n*-Butylaminoboracyclopentane.** Substantial warming up of the reaction mixture was observed when 3.0 g (0.40 mole) of *n*-butylamine was added at room temperature to 5.1 g (0.033 mole) of 1-*n*-butylthioboracyclopentane. Subsequent fractional distillation of the mixture in vacuo gave 3.4 g (74%) of 1-*n*-butylaminoboracyclopentane with b. p. 63-64° (9 mm);  $d_4^{20}$  0.8588;  $n_D^{20}$  1.4730; found MR 45.42; calculated MR 44.90. Found: C 69.06, 68.96; H 13.25, 13.23; B 7.99, 7.76%.  $\text{C}_8\text{H}_{18}\text{BN}$ . Calculated: C 69.09; H 13.05; B 7.78%.

**1-*n*-Butoxyboracyclopentane.** A solution of 6.6 g (0.042 mole) of 1-*n*-butylthioboracyclopentane in 15 ml of ether was cooled to -70° and then a solution of 3.7 g (0.05 mole) of *n*-butyl alcohol in 15 ml of ether was added in 1 hr. The reaction was accompanied by the evolution of heat. Then the mixture was warmed up to room temperature, and the solvent and butyl mercaptan were removed by vacuum-distillation. Fractional distillation of the residue gave 2.6 g of 1-*n*-butoxyboracyclopentane, b. p. 64-70° (11 mm). After redistillation the compound had b. p. 56-58° (9 mm);  $d_4^{20}$  0.8801;  $n_D^{20}$  1.4502; found MR 42.78; calculated MR 42.87. Found: C 68.58, 68.81; H 12.01, 12.09; B 7.84, 7.81%.  $\text{C}_8\text{H}_{17}\text{BO}$ . Calculated: C 68.61; H 12.24; B 7.73%.

## SUMMARY

1. 1-*n*-Butylthioboracycloalkanes are obtained when dienic hydrocarbons are reacted with the polymer of *n*-butylthioborane.
2. When reacted with amines or alcohols, the butylthio group in 1-*n*-butylthioboracyclopentane is replaced by the corresponding alkylamino or alkoxy group.

#### LITERATURE CITED

1. B. M. Mikhallov and T. A. Shchegoleva, Doklady Akad. Nauk SSSR 131, 843 (1960).
2. B. M. Mikhallov, T. A. Shchegoleva, E. M. Shashkova, and V. D. Sheludyakov, Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk 1961, 1163.
3. K. Torsell, Acta Chem. Scand. 8, 1779 (1954).
4. S. Clark, Chem. and Engng. News 36, N 17, 56 (1958).
5. R. Köster, Angew. Chem. 71, 520 (1959).
6. B. M. Mikhallov and V. A. Dorokhov, Doklady Akad. Nauk SSSR 133, 119 (1960).
7. M. Hawthorne, J. Amer. Chem. Soc. 82, 748 (1960).
8. H. Brown and B. Rao, J. Amer. Chem. Soc. 78, 5694 (1960).
9. Ya. L. Gol'dfarb and L. M. Smorgonskii, Zhur. Obshchei Khim. 8, 1516 (1938).

---

All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

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# REDUCTION OF METHYLCYCLOHEXANONES WITH DIISOBUTYLALUMINUM HYDRIDE

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A number of papers [1-7] have been devoted to the stereochemistry of the reduction of methylcyclohexanones to methylcyclohexanols using lithium aluminum hydride. Recently Hückel and co-workers [3] and Dauben and co-workers [4] have carried out careful studies, which have brought a definite clarity to the problem, since prior to this various authors obtained different ratios of the cis- and trans-isomers when the methylcyclohexanones were reduced to the methylcyclohexanols. Earlier, to explain the results obtained in the reduction of the methylcyclohexanones, Dauben and co-workers [5] expressed the theory that the ratio of the formed cis- and trans-isomers of the methylcyclohexanols depends on two factors: steric ("Steric approach control") and energetic, the latter including the relative stability of the possible reaction products ("product development control").

It seemed of interest to us to verify this theory for the case of the reduction of the methylcyclohexanones using diisobutylaluminum hydride  $(\text{iso-C}_4\text{H}_9)_2\text{AlH}$ , where, obviously, the influence of the steric factor should be manifested more clearly, since in this compound the aluminum is attached to more bulky substituents than in the case of lithium aluminum hydride. In its reducing ability diisobutylaluminum hydride should lie close to lithium aluminum hydride, while for studying the reduction reaction it possesses the advantage that it is easily available in the pure state. We studied the reduction of 2-methyl-, 3-methyl- and 4-methylcyclohexanones at various temperatures and in a number of solvents (ether, toluene, hexane). The obtained results are summarized in the table. For comparison, we have included in the table the data of other authors on the reduction of the methylcyclohexanones with lithium aluminum hydride.

Amount of Methylcyclohexanol Isomers

Compound	Solvent	Reaction temperature, °C	Amount, %		
			of trans-isomer		of trans-isomer in equilibrium mixture
			using $(\text{iso-C}_4\text{H}_9)_2\text{AlH}$	using $\text{LiAlH}_4$	
2-Methylcyclohexanone	Ether	-60	43 (47)*	70[4], 59[3]	85[4], 83[3]
	"	30	44 (48)*		
3-Methylcyclohexanone	"	60	18	13[4], 7[3]	22 [7]
		30	18		
4-Methylcyclohexanone	"	-60	67	84[4], 80[7]	71[4], 70[7]
		0	68		
	Hexane	0	60		
	Toluene	100	56		
	Without solvent	130	56		

\* Amount of the trans-isomer in % based on the density values  $d^{30}_4$ , determined by Hückel [3].

As can be seen from the table, the greatest difference in the ratio of the isomers when comparing reduction with diisobutylaluminum hydride vs. reduction with lithium aluminum hydride is observed for the case of 2-methylcyclohexanone. The greatest deviation of the obtained composition of the isomeric alcohols from the equilibrium

composition is also observed in this case, in which connection the less stable *cis*-isomer is present in the greater amount. This result definitely suggests the presence of the steric effect in the reduction of 2-methylcyclohexanone and is in agreement with the theory expressed by Dauben and co-workers [4].

When 3-methylcyclohexanone and 4-methylcyclohexanone are reduced with diisobutylaluminum hydride the composition of the mixed isomers lies very close to the equilibrium composition, which is also in agreement with the postulation of Dauben and co-workers, since in the case of unhindered ketones the main factor is the energetic. When 4-methylcyclohexanone is reduced with diisobutylaluminum hydride the amount of the stable *trans*-isomer is considerably less than when reduction is with lithium aluminum hydride. When using diisobutylaluminum hydride for reduction we did not observe the temperature to have any noticeable effect, whereas according to the data of Hückel and co-workers [3] such an effect does exist in the case of lithium aluminum hydride. The solvent does have some effect on the composition of the mixed isomers when reduction is with diisobutylaluminum hydride. Thus, the reduction of 4-methylcyclohexanone in toluene, hexane, or without solvent, yields less of the more stable *trans*-isomer than when reduction is in ether.

#### EXPERIMENTAL

The starting methylcyclohexanones had the following constants: 2-methylcyclohexanone (purified through the semicarbazone) — b. p. 83° (48 mm);  $n_D^{30}$  1.448;  $d_4^{30}$  0.9161; f. p. -13.1°; 3-methylcyclohexanone (purified through the semicarbazone) — b. p. 62-63° (20 mm);  $n_D^{30}$  1.4438;  $d_4^{20}$  0.9147;  $d_4^{20}$  0.9067; f. p. -74.5°; 4-methylcyclohexanone — b. p. 64-65° (20 mm);  $n_D^{30}$  1.4428;  $d_4^{30}$  0.9073; f. p. -42.8°.

Reduction of methylcyclohexanones. The isomer ratio in the mixed methylcyclohexanols was established by measuring the density. The following density values  $d_4^{30}$  were taken: for *cis*-2-methylcyclohexanol 0.9274, *trans* 0.9174 [8]; for *cis*-3-methylcyclohexanol 0.9065, *trans* 0.9138 [9]; for *cis*-4-methylcyclohexanol 0.9173, *trans* 0.9040 [10]. In all of the experiments the amount of starting ketone in the obtained methylcyclohexanol did not exceed 0.5%.

2-Methylcyclohexanol. With stirring and cooling to -60°, a solution of 8.5 g (0.076 mole) of the ketone in 12 ml of dry ether was added to 13.8 g (0.097 mole) of diisobutylaluminum hydride in 24 ml of ether. After all of the ketone had been added the reaction mixture was kept at -60° for another 12 hr, and then decomposed with 5% H<sub>2</sub>SO<sub>4</sub>. We obtained 7.8 g (91% of theory) of mixed isomeric 2-methylcyclohexanols with b. p. 73-74.5° (20 mm);  $d_4^{30}$  0.9231.

#### SUMMARY

The stereochemistry of the reduction of the 2-, 3- and 4-methylcyclohexanones by diisobutylaluminum hydride was studied and it was found that in the case of 2-methylcyclohexanone the steric factor exerts an influence on the reduction course.

#### LITERATURE CITED

1. D. S. Noyce and D. B. Denney, J. Am. Chem. Soc. **72**, 5743 (1950).
2. K. D. Hardy and R. J. Wicker, J. Am. Chem. Soc. **80**, 640 (1958).
3. W. Hückel and A. Hubele, Liebigs Ann. Chem. **613**, 27 (1958).
4. W. G. Dauben and R. E. Bozak, J. Organ. Chem. **24**, 1596 (1959).
5. W. G. Dauben, G. J. Fonken, and D. S. Noyce, J. Am. Chem. Soc. **78**, 2579 (1956).
6. R. Cornubert and M. Lafont-Lemoine, K. Nadjme-Abadi, Compt. rend. **237**, 469 (1953).
7. E. L. Eliel and R. S. Ro, J. Am. Chem. Soc. **79**, 5992 (1957).
8. L. M. Jackman, A. K. Macbeth, and J. A. Mills, J. Chem. Soc. **1949**, 2641.
9. W. Hückel and J. Kurz, Ber. **91**, 1290 (1958).
10. L. M. Jackman, A. K. Macbeth, and J. A. Mills, J. Chem. Soc. **1949**, 1718.

## THERMAL ALKYLATION OF CYCLOPENTANE WITH OLEFINS

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Up to now the alkylation of cycloalkane hydrocarbons has remained almost completely unstudied. Pines and Ipatieff [1] studied the alkylation of methylcyclopentane with olefins in the presence of either  $H_2SO_4$  (100%) or HF. The process went in a very complex manner. For example, in the reaction with butylenes, instead of the expected disubstituted cyclopentane derivative, the trisubstituted 1,3-dimethyl-5-ethyl- and 1,3-dimethyl-4-ethylcyclohexanes were obtained. Under analogous conditions, Mamedaliev with Kuliev [2] and Mamedova [3] alkylated methyl-, ethyl-, and isopropylcyclohexane with propylene and with butylene. The obtained alkylates contain 20-30% (60-70%, based on the converted cycloalkane) of direct alkylation products. However, the unsubstituted cyclopentane and cyclohexane are not alkylated under these conditions.

In the present paper the direct alkylation of cyclopentane with ethylene and with propylene, employing high temperatures and pressure, was accomplished for the first time. The principal reaction products were isolated and characterized, and a study was made of the effect of temperature and pressure on the course of the process.

### EXPERIMENTAL

The experiments were run in an apparatus of the flow type [4]. A liquid pump was used to feed the mixture of cyclopentane and olefin into the reactor, which was heated in an electric furnace. The reactor, having a volume of 120 ml, was filled with pieces of quartz. The catalyzate was discharged continuously through a fine control valve. The starting cyclopentane had: b. p. 48.5-49.5°;  $n_D^{20}$  1.4072;  $d_4^{20}$  0.7456. The ethylene contained 6% ethane, and the propylene contained 13% propane. The alkylates were fractionated through a very efficient column. Both the isolated wide and narrower fractions were analyzed by the method of gas-liquid chromatography, using a column 2.5 m long and temperatures of 100 and 140°; dibutyl sebacate was used as the stationary phase. The apparatus was quantitatively calibrated in advance using pure hydrocarbons. The low-boiling cracked products and the high-boiling residue, contained in the alkylate, were not analyzed.

Alkylation with ethylene. From the table it can be seen that the reaction goes even at 350° and a pressure of 200 atm. Both the yield of alkylate and the degree of conversion increase with increase in the temperature and pressure. The ethylene taken for reaction was absorbed completely at a temperature of 450°. The chromatogram of one of the catalyzates, including the hydrocarbons up to  $C_9$ , is given in Fig. 1. The curve for the fractional distillation of this catalyzate is also given in Fig. 1. The principal reaction products are ethylcyclopentane (peak III), diethylcyclopentanes (peaks IV and V), and butylcyclopentane (peak VI). The horizontal portion on the distillation curve corresponds to each of these peaks. After removal of the cyclopentane from the alkylate, the following fractions were isolated by fractional distillation: I - monoethylcyclopentane (b. p. 100-105°), and II - diethylcyclopentane (b. p. 145-160°). The unsaturation of the alkylate was low, for example, in the experiment at 200 atm and 450° the bromine number of fraction I was 4, and that of fraction II was 15. After removal of the unsaturates by chromatography on silica gel, fraction I had: b. p. 101.9-102.3° (739 mm);  $n_D^{20}$  1.4204;  $d_4^{20}$  0.7658. According to the literature data [5] for ethylcyclopentane: b. p. 103.47°;  $n_D^{20}$  1.4198;  $d_4^{20}$  0.7665. The chromatogram of fraction I had only one peak, from the effluent time coinciding with pure ethylcyclopentane. After removal of the unsaturates, fraction II boiled mainly in the range 148-154°;  $n_D^{21.5}$  1.4293;  $d_4^{20}$  0.7826; the properties of this fraction correspond to diethylcyclopentane. From the literature data [5], the constants of the four isomers of diethylcyclopentane vary in the range: b. p. 147.5-153.5°;  $n_D^{20}$  1.4274 - 1.4356;  $d_4^{20}$  0.7831 - 0.8027.

From the table it can be seen that the yield of ethylcyclopentane reaches 36% of the weight of alkylate and 65% of the weight of the wide fraction. The chromatogram of the 148-154° fraction is shown in Fig. 2. Apparently,

Experimental conditions				Conversion of olefin, %	Yield of alkylate based on taken olefin, wt. %	Amount of fractions in alkylate, wt. %				Amount of alkylcyclopentanes in wide fraction,* %	
temperature, °C	pressure, atm	ratio C <sub>5</sub> H <sub>10</sub> : olefin	space velocity of mixture, hr <sup>-1</sup>			monoalkylcyclopentane	dialkylcyclopentane	high-boiling residue	monoalkylcyclopentane	dialkylcyclopentane	
Alkylation with ethylene											
350	200	2,9	1,1	42	110	—	—	—	—	—	—
400	200	2,8	0,9	58	104	—	—	—	—	65	19
450	100	2,4	0,76	100	145	27	10	40	—	60	30
450	200	1,6	0,95	100	165	30	18	35	—	—	—
450	200	2,4	0,46	94	160	31	17	35	—	63	25
450	450	2,1	1,45	100	177	36	10	41	—	63	26
500	200	2,9	1,0	98	248	—	—	30	—	58	22

Alkylation with propylene												
450	200	5,0	1,7	100	147	26	—	43	—	—	—	—
450	200	3,5	0,80	84	220	29	—	27	—	—	—	—
450	450	2,4	0,83	—	157	30	—	25	—	50,5	—	10**
450	450	4,6	0,66	97,5	270	—	—	—	—	—	—	—
450	450	2,2	0,48	95,0	162	22	—	33	—	—	—	—

\* Determination by the chromatographic method in the fractions:  $C_6-C_9$  for the reaction using ethylene, and  $C_6-C_{11}$  for the reaction using propylene.

\*\* Methylcyclopentane (6%) and ethylcyclopentane (7%) were also identified.

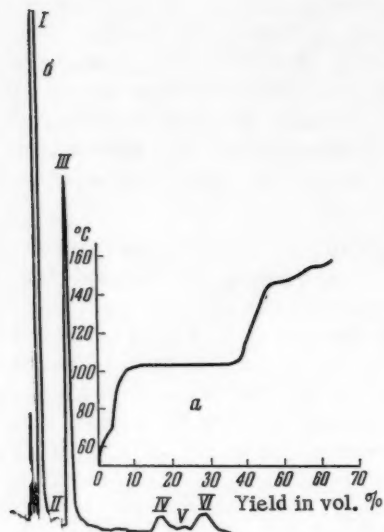


Fig. 1a.

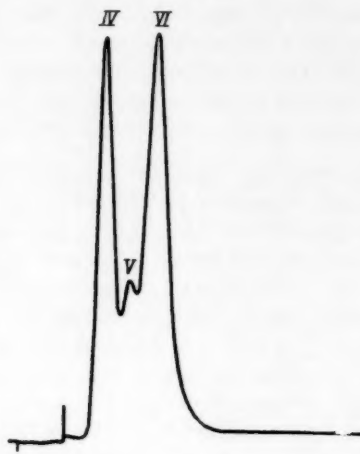


Fig. 2.

Fig. 1a. Curve for the fractionation of the alkylate obtained from cyclopentane and ethylene (450°, 200 atm). 1b) Chromatogram of the product from the alkylation of cyclopentane with ethylene: I) cyclopentane; II) methylcyclopentane; III) ethylcyclopentane; IV and V) diethylcyclopentanes; VI) butylcyclopentane.

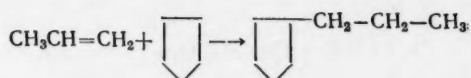
Fig. 2. Chromatogram of 148-154° fraction.



the left and middle peaks correspond to isomers of diethylcyclopentane, while the right peak, from the effluent time, coincides with pure n-butylcyclopentane. The addition of pure n-butylcyclopentane of the analyzed sample increased the area of the right peak. The narrower fractions isolated from fraction II give a similar picture, differing only in that the area of the right peak increases with increase in the boiling point of the fraction.

Alkylation with propylene is more difficult than with ethylene, and the propylene was not absorbed at 100 atm. From the alkylates of the experiments run at 200-450 atm of pressure we isolated by fractional distillation the low boiling cracked products (up to 33% of the alkylate), a propylcyclopentane fraction, and a higher boiling residue. After chromatographing on silica gel this fraction had b. p. 128.2-129.2° (735 mm);  $n_D^{20}$  1.4264;  $d_4^{20}$  0.7736. According to the literature [5] the constants for n-propylcyclopentane are: b. p. 130.95°;  $d_4^{20}$  0.7763;  $n_D^{20}$  1.4263. According to the effluent time, the main peak of this fraction on the chromatogram corresponds to n-propylcyclopentane. From the residue, after removal of the unsaturates and high boilers, we isolated a fraction with b. p. 189-193°;  $n_D^{20}$  1.4392;  $d_4^{20}$  0.7958, which is probably a mixture of isomeric dipropylcyclopentanes, not reported in the literature.

Recently [6] it was shown by us that cyclohexane during thermal alkylation adds to the terminal unsaturated atom of the olefin (propylene, isobutylene). In the present study it was found that cyclopentane also reacts with propylene in a similar manner:



#### SUMMARY

1. The alkylation of cyclopentane with ethylene and propylene under pressure was accomplished for the first time, and a study was made of the influence of the experimental conditions on the course of the process.
2. During thermal alkylation, cyclopentane adds to the terminal unsaturated C-atom of propylene.

#### LITERATURE CITED

1. H. Pines and N. Ipatieff, J. Amer. Chem. Soc. **67**, 1631 (1945).
2. Yu. G. Mamedaliev and A. Kullev, Doklady Akad. Nauk SSSR **88**, 471 (1953).
3. Yu. G. Mamedaliev and Z. A. Mamedova, Doklady Akad. Nauk SSSR **112**, 1063 (1957).
4. L. Kh. Freidlin, A. A. Balandin, and N. M. Nazarova, Doklady Akad. Nauk SSSR **96**, 1011 (1954).
5. R. D. Obolentsev, Physical Constants of Hydrocarbons of Liquid Fuels and Oils [in Russian] (State Press of Technical Literature on Building, Moscow-Leningrad, 1953).
6. N. M. Nazarova and L. Kh. Freidlin, Doklady Akad. Nauk SSSR **137**, 1125 (1961).

All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. Some or all of this periodical literature may well be available in English translation. A complete list of the cover-to-cover English translations appears at the back of this issue.

# AMINOTRIAZOLES IN THE MANNICH REACTION

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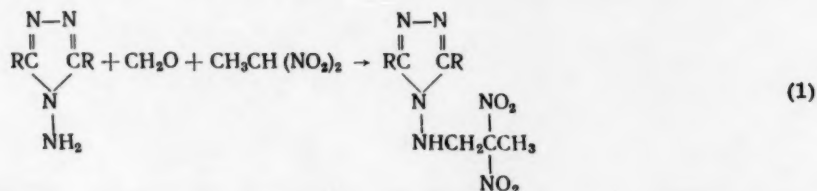
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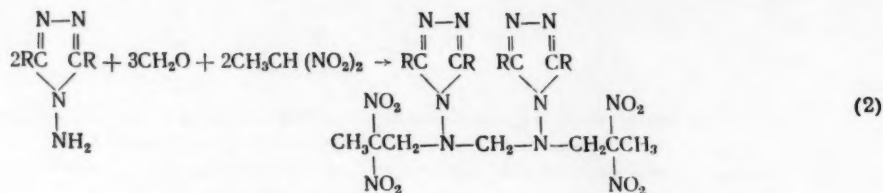
Continuing our study of the behavior of various heterocyclic amines in the Mannich reaction, we investigated the condensation of 4-amino-1,2,4-triazole and certain 3,5-dialkyl-4-aminotriazoles with formaldehyde and gem-dinitroethane to yield the corresponding 4-(2,2-dinitropropyl)amino-1,2,4-triazoles:



where R = H, CH<sub>3</sub>, or C<sub>2</sub>H<sub>5</sub>.

During the course of the work we studied the influence of the reaction conditions (temperature and ratios of the reactants) on the yields of the condensation products. It was shown that the best conditions for the condensation of 4-amino-1,2,4-triazole, and also of the 3,5-dimethyl-4-amino- and 3,5-diethyl-4-amino-1,2,4-triazoles, with formaldehyde and gem-dinitroethane are a temperature of 50-60° and no catalyst. Under these conditions the corresponding 4-(2,2-dinitropropyl)amino-1,2,4-triazoles, representing white crystalline compounds, readily soluble in many organic solvents (acetone, methanol, ethyl acetate), are obtained in high yields (75-86%). The optimum ratio of the reactants is a 25-50% excess of the amine with an equimolar ratio of the formaldehyde and gem-dinitroethane. Using an excess of the gem-dinitroethane (from 5 to 100%) yields an oil, from which the condensation product could not be isolated.

It could be postulated that when excess formaldehyde is used the reaction goes in accordance with the following scheme:



However, the experiments revealed that even with a 100% excess of formaldehyde the condensation goes only in accordance with scheme (1).

## EXPERIMENTAL

4-Amino-1,2,4-triazole [2]. The compound was obtained by heating formic acid with hydrazine hydrate at 200-210° for 4-5 hr; yield 80%; m. p. 76-77° (from absolute alcohol).

3,5-Dimethyl-4-amino-1,2,4-triazole [2]. Obtained by heating acetic acid and hydrazine hydrate at 220-230° for 5 hr; yield 75%; m. p. 195-196° (from alcohol). Literature data: m. p. 196.5-197.5°.

3,5-Diethyl-4-amino-1,2,4-triazole [2]. Obtained by heating propionic acid and hydrazine hydrate at 220-230° for 5 hr; yield 68%; m. p. 165.6-166.5°.

Condensation of 4-amino-1,2,4-triazole with formaldehyde and gem-dinitroethane. With cooling to 0° and stirring, a solution of 10.2 g (0.12 mole) of 4-amino-1,2,4-triazole in 5 ml of water was added to 9.4 ml of a 32% aqueous solution of formalin (0.1 mole). The temperature rose rapidly to 15°. Then 12 g (0.1 mole) of gem-dinitroethane was added at 5°, after which the mixture was heated at 50-55° for an hour. The crystals obtained on cooling to room temperature were filtered and dried in the air to give 16.2 g of 4-(2,2-dinitropropyl)amino-1,2,4-triazole; colorless crystals, readily soluble in methanol and acetone; m. p. 140.5° (from alcohol); yield 75%. Found: C 27.80, 27.68; H 3.71, 3.64; N 38.95, 38.74%.  $C_5H_8O_4N_6$ . Calculated: C 27.78; H 3.70; N 38.88%.

Condensation of 3,5-dimethyl-4-amino-1,2,4-triazole with formaldehyde and gem-dinitroethane. With cooling to 0° and stirring, a solution of 4 g of 3,5-dimethyl-4-amino-1,2,4-triazole (0.035 mole) in 8 ml of water was added to 2.82 ml of a 32% aqueous solution of formalin (0.03 mole). The temperature rose to 12°. Then 3.6 g (0.03 mole) of gem-dinitroethane was added at 4-5° and the mixture was heated at 55-60° for 1 hr. After cooling, the crystals were filtered, washed with ether, and dried in the air. We obtained 4.8 g of 3,5-dimethyl-4-(2,2-dinitropropyl)amino-1,2,4-triazole; white crystals, readily soluble in methanol, alcohol, and acetone; m. p. 94° (from water). An additional 1.3 g of the compound was isolated from the mother liquor; total yield 83.5%. Found: C 34.33, 34.39; H 5.07, 5.00; N 34.52, N 34.64%.  $C_7H_{12}O_4N_6$ . Calculated: C 34.43; H 4.91; N 34.41%.

Condensation of 3,5-diethyl-4-amino-1,2,4-triazole with formaldehyde and gem-dinitroethane. With cooling to 0° and stirring, a solution of 2.1 g (0.015 mole) of 3,5-diethyl-4-amino-1,2,4-triazole in 10 ml of water was added to 0.94 ml of a 32% aqueous solution of formalin (0.01 mole). The temperature rose to 15°. Then 1.2 g (0.01 mole) of gem-dinitroethane was added at 5° and the mixture was heated at 60° for an hour. On cooling to room temperature the turbid solution deposited an oil, which crystallized after standing for 2-3 days. The crystals were filtered and dried in the air to give 1.8 g of 3,5-diethyl-4-(2,2-dinitropropyl)amino-1,2,4-triazole as colorless prisms, readily soluble in acetone, alcohol, methanol, dioxane, ethyl acetate, and benzene; m. p. 99-100° (from benzene) and 103° (from water).

An additional 0.55 g of the compound was isolated from the mother liquor; total yield 86.4%. Found: C 39.46, 39.55; H 5.91, 5.88; N 30.41, 30.30%.  $C_9H_{16}O_4N_6$ . Calculated: C 39.70; H 5.88; N 30.88%.

#### SUMMARY

4-(2,2-Dinitropropyl)amino-1,2,4-triazoles are the products obtained by the condensation of 4-amino-1,2,4-triazole and its homologs with formaldehyde and gem-dinitroethane. Condensation products containing two molecules of the amine were not found.

#### LITERATURE CITED

1. S. S. Novikov, Z. Ya. Lapshina, V. A. Rudenko, and L. S. Semenenok, *Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk* 1960, 1302.
2. R. Herbst and J. A. Garrison, *J. Org. Chem.* **18**, N 7-8, 872 (1953).

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. Some or all of this periodical literature may well be available in English translation. A complete list of the cover-to-cover English translations appears at the back of this issue.

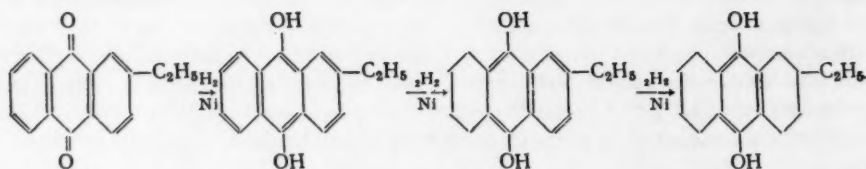
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# THE SELECTIVITY OF THE HYDROGENATION OF 2-ETHYLANTHRAQUINONE OVER NICKEL CATALYST

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As is known, quinones of the anthraquinone series easily add hydrogen not only to the quinone groups, but also to the aromatic bonds in the side rings. Here, together with the hydroquinone, both the tetrahydroquinone and octahydroquinone can be formed.



In the present paper we studied the influence of temperature and some other factors on the rate and selectivity of this reaction on nickel. The hydrogenation was run in a duck [horizontal glass vessel with vertical openings at each end] in conventional manner with vigorous mixing (800 r.p.m.). The selective nickel catalyst was prepared by leaching Ni:Al alloy (50:50) at 20° and subsequent heating at 100° [1]. We selected dioxane as the solvent, in which the hydrogenation is not as selective as in polar solvents (alcohol, dimethylformamide). For each experiment we took 2.37 g of the quinone in 30 ml of dioxane and 0.30 g of freshly prepared catalyst. In contrast to previous work [2, 3], in the present study we used a catalyst of average activity, the specific activity of which remained constant with increase in its amount. The absorption rate of the first mole of hydrogen was only 2-3 times as fast as the absorption rate of the second mole.

The kinetic curves for the hydrogenation of 2-ethylanthraquinone are given in Fig. 1. From Fig. 1 it can be seen that in the entire temperature range from 20 to 80° the reaction does not stop when one mole of hydrogen has been absorbed (formation of the hydroquinone); one side ring of the quinone is hydrogenated at a faster rate. The second ring begins to hydrogenate after the absorption of three moles of hydrogen, but here the reaction rate is much slower.

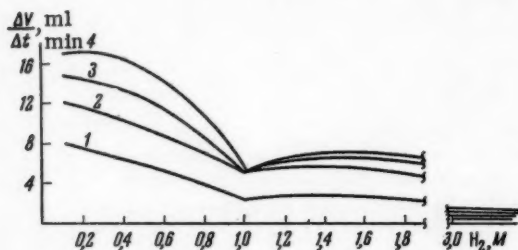


Fig. 1. Kinetic curves of the hydrogenation of 2-ethylanthraquinone in dioxane at various temperatures: 1) 20°; 2) 40°; 3) 60°; 4) 80°.

The dependence of the hydrogenation rates of the quinone groups and the aromatic ring of 2-ethylanthraquinone on the temperature is shown in Fig. 2a. The rates at the time 0.5 mole and 1.5 moles of hydrogen had been absorbed were taken for comparison. From Fig. 2a it can be seen that from 20 to 80° the hydrogenation rate of the quinone groups (curve 1) increases linearly with increase in the temperature. For the second stage (curve 2) some reduction in the rate of increase of the reaction rate is observed when the temperature is increased from 60 to 80°.

The nonexponential dependence of the rates of both reactions on the temperature is probably explained by a decrease in the concentration of active hydrogen on the catalyst surface with increase in the temperature.



The extent to which the quinone groups were selectively hydrogenated was determined by the amount of 2-ethyltetrahydroanthrahydroquinone formed during the absorption of the first mole of hydrogen. For this purpose samples of the catalyzate were removed during the course of reaction. After oxidation, these samples were subjected to polarographic analysis. It proved that under the studied conditions varying the temperature in the range 20-80° is essentially without effect on the selectivity of the hydrogenation of 2-ethylanthraquinone. At all of the temperatures, the amount of tetrahydroanthrahydroquinone present in the catalyzate at the end of the absorption of the first mole of hydrogen is about 4-8%, and this amount is formed mainly after the absorption of the first 0.5 mole of hydrogen (Fig. 2b).

It should be remembered that the vapor pressure of the dioxane solvent is increased substantially when the temperature is raised (about 400 mm of Hg at 80°), and this results in a corresponding decrease in the partial pressure of the hydrogen. This can explain why the selectivity is not impaired when the rate of increase in the reaction rate slows up with increase in the temperature.

If judging by the concentration of 2-ethyltetrahydroanthrahydroquinone in the solution (4-8%), the selectivity of the process is not changed noticeably when the amount of catalyst is increased from 0.1 to 5 g (50-fold). It should be mentioned that with large amounts of catalyst the concentration of the quinones in the solution decreases (by 20%) due to adsorption on the catalyst. The distribution of the quinones between the solution and the catalyst surface was not investigated.

As had already been indicated in [2, 3], in the presence of skeletal nickel catalyst both the rate and the selectivity of the hydrogenation of the quinone groups in 2-ethylanthraquinone depend essentially on the nature of the solvent. In polar solvents (alcohol, dimethylformamide) the hydrogenation rate at 20° of the quinone groups in 2-ethylanthraquinone is higher, while the hydrogenation rate of its side rings is lower, than in dioxane. Now it was established by us that dimethylformamide exerts the same effect when 2-ethylanthraquinone is hydrogenated at a higher temperature (60°). From Fig. 3 it can be seen that at this temperature the reaction rate during the first stage is more than 3 times as fast in dimethylformamide as in dioxane, whereas the aromatic ring is practically not hydrogenated. Less than 1% of the tetrahydroquinone was formed after the absorption of one mole of hydrogen and additional shaking with the catalyst for 7 hr.

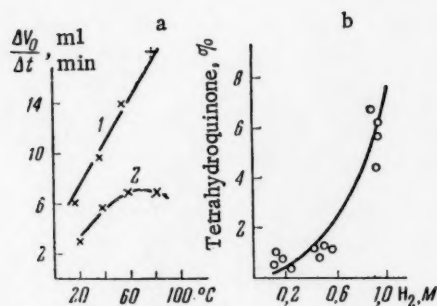


Fig. 2a. Dependence of the reaction rates on the temperature: 1) hydrogenation of quinone groups; 2) hydrogenation of ring. 2b) Accumulation of the tetrahydroquinone during the absorption of the first mole of hydrogen.

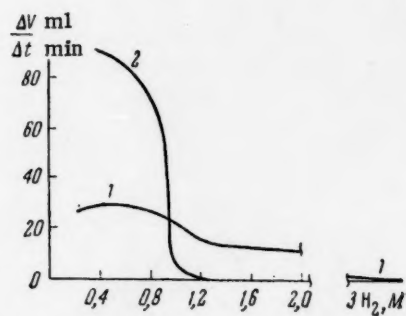


Fig. 3. Kinetic curves of the hydrogenation of 2-ethylhydroquinone at 60°: 1) in dioxane; 2) in N,N-dimethylformamide.

Previously it had been established that the selectivity of the skeletal nickel catalyst is increased by treatment with steam under pressure [4]. We ran an analogous experiment and found that 2-ethylanthraquinone absorbs practically only one mole of hydrogen, i.e., the ring of the quinone is not hydrogenated, when using a catalyst that had been treated with steam at 190-200° for 1 hr. At the same time, the hydrogenation rate of the quinone groups decreases due to the general deactivation of the catalyst.

#### SUMMARY

1. The selectivity of the hydrogenation of 2-ethylanthraquinone on skeletal nickel catalyst in dioxane solution is practically independent of both the amount of catalyst and the temperature in the interval 20-80°.
2. Steam-treated nickel catalyst selectively catalyzes the hydrogenation of 2-ethylanthraquinone to the hydroquinone.

#### LITERATURE CITED

1. A. Pavlic and H. Adkins, J. Amer. Chem. Soc. 68, 1471 (1946).
2. L. Kh. Freidlin and E. F. Litvin, Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk 1960, 734.
3. L. Kh. Freidlin, E. F. Litvin, and V. E. Ditsent, Doklady Akad. Nauk SSSR 131, 1362 (1960).
4. L. Kh. Freidlin, Problemy Kinetiki i Kataliza 10, 187 (1960).

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

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USE OF TRANS-1-VINYL-6-ACETOXY- AND TRANS-1-VINYL-6-ETHYLENEDIOXY-9-METHYL- $\Delta^1$ -OCTALINS IN  
DIENE SYNTHESIS REACTIONS

V. F. Kucherov and I. A. Gurvich

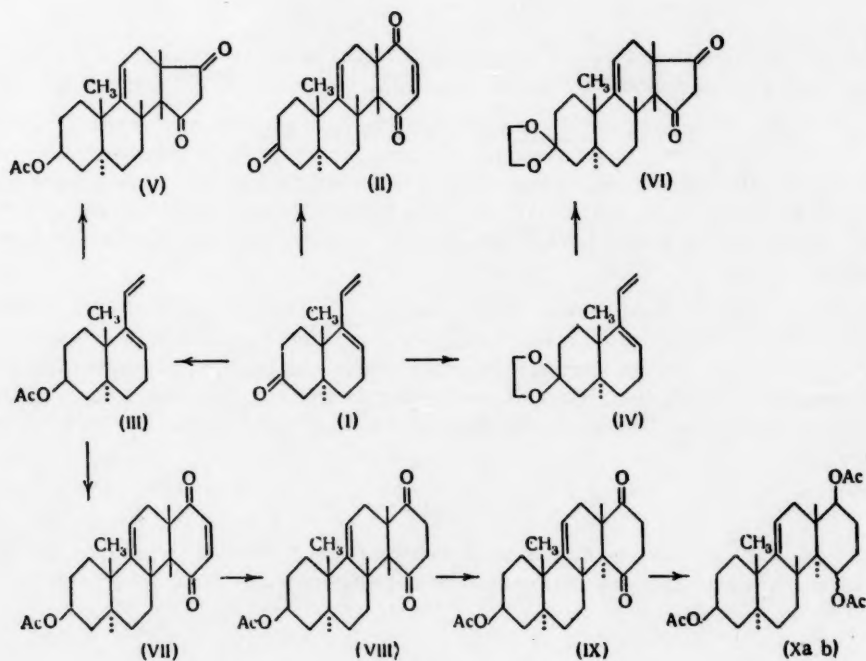
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As was shown in one of the preceding articles [1], the condensation of trans-1-vinyl-6-keto-9-methyl- $\Delta^1$ -octalin (I) with quinone gives, as the main reaction product, the adduct (II) with the angular methyl group in the cis-position relative to the hydrogen atoms on C<sub>8</sub>, C<sub>13</sub>, and C<sub>14</sub>. Owing to the presence of a free keto group, however, this diene could not be used directly in diene condensations with cyclopentenedione-1,3, as was done earlier in the case of 1-vinyl-6-methoxy-3,4-dihydronaphthalene [2]. In order to protect the oxygen function in diene (I), we prepared its derivatives (III) and (IV), which also was studied in diene-synthesis reactions. It was found that these dienes (without isolation in pure form) could be condensed relatively easily with cyclopentenedione-1,3, as a result of which individual adducts (V) and (VI) were obtained; the structures of the latter must correspond to derivatives of 18-nor-14-iso- $\Delta^9(11)$ -androstene-15,17-dione. The IR spectra of these adducts show the presence of a completely enolized keto group in ring D. Since adducts (V) and (VI) were isolated as the main reaction products of the diene synthesis, their configuration may be considered analogous to that of adduct (II). In order to confirm that the same regularities of steric directivity of diene synthesis, which apply to the original 1-vinyl-6-keto-9-methyl- $\Delta^1$ -octalin (I), are characteristic of dienes (III) and (IV), we studied the condensation of diene (III) with quinone.



On reduction of the resulting mixture of adducts (VII) with zinc in acetic acid we isolated diketoacetate (VIII) as the main reaction product; its configuration was proved by conversion to the isomeric triacetates (Xa, b), described earlier [3]. The results obtained show that in the condensation of diene (III) with quinone the main product is the isomeric adduct (VII) whose configuration is identical with that of adduct (II), described earlier [1]. This provides sufficient grounds for considering that adducts (V) and (VI) are derivatives of 18-nor-14-isoandrostene, and their configuration corresponds to the *cis*-arrangement of the C<sub>8</sub>, C<sub>13</sub>, and C<sub>14</sub> hydrogen atoms relative to the angular methyl group.

#### EXPERIMENTAL

DL-18-nor-14-iso-3-acetoxy- $\Delta^{9(11)}$ -androstene-15,17-dione (V). To 1.9 g of crude diene (III), prepared through the reduction of diene (I) with lithium borohydride and subsequent acetylation, a solution of 0.9 g of cyclopentenone in 7 ml of benzene was added. After standing for 9 days at room temperature 0.7 g of the adduct, m. p. 207-208°, was filtered out. After crystallization from aqueous methanol there was obtained 0.55 g of diketoacetate (V), m. p. 211-212°;  $\nu$  (in CHCl<sub>3</sub>) 1722 (K 1325), 1575 cm<sup>-1</sup> (K 1593). Found: C 72.68, 72.98; H 8.12, 8.17%. C<sub>20</sub>H<sub>26</sub>O<sub>4</sub>. Calculated: C 72.70; H 7.93%.

About 300 mg of a lower-melting product was isolated from the benzene solution; it was not further studied.

DL-18-nor-14-iso-3-ethylenedioxy- $\Delta^{9(11)}$ -androstene-15,17a-dione (VI). To 1 g of crude diene (IV), prepared by boiling diene (I) with ethylene glycol in benzene in the presence of *p*-toluenesulfonic acid, a solution of 0.5 g of cyclopentenone in 4 ml of benzene was added, and the mixture was left at room temperature. After 2 days 1.18 g of separated-out crystals was filtered out; they did not have a sharp melting point, but partially liquified at 205-211°. Recrystallization from methanol gave 360 mg of diketone (VI), m. p. 227-228°;  $\nu$  (in CHCl<sub>3</sub>) 1739 cm<sup>-1</sup> (K 795). Found: C 72.68, 72.75; H 7.77, 7.79%. C<sub>20</sub>H<sub>26</sub>O<sub>4</sub>. Calculated: C 72.70; H 7.93%. No other individual products could be isolated from the mother liquors.

DL-18-nor-D-homo-14-iso-3-acetoxy- $\Delta^{9(11)}$ -androstene-15,17a-dione (VIII). To 1 g of crude diene (III), a solution of 0.49 g of quinone in 7 ml of benzene was added, and the mixture was left at room temperature. After a week the benzene was distilled off, ether added to the residue, and 0.9 g of a mixture of adducts (VII), m. p. 132-134°, filtered out. This mixture was dissolved in acetic acid and reduced with 0.7 g of zinc dust. There was obtained 0.67 g of crystals with m. p. 162-165°, which on recrystallization from methanol gave 480 mg of diketone (VIII), m. p. 182-183°;  $\nu$  (in CHCl<sub>3</sub>) 1717 cm<sup>-1</sup> (K 2940). Found: C 73.05, 73.02; H 7.88, 8.11%. C<sub>21</sub>H<sub>28</sub>O<sub>4</sub>. Calculated: C 73.22; H 8.19%.

From the mother liquor about 50 mg of crystals of the second isomer (VIIIa), m. p. 156-157° (from aqueous methanol), was isolated. Found: C 72.78; H 8.32%. C<sub>21</sub>H<sub>28</sub>O<sub>4</sub>. Calculated: C 73.22; H 8.19%.

DL-18-nor-D-homo-3-acetoxy- $\Delta^{9(11)}$ -androstene-15,17a-dione (IX). A solution of 0.2 g of diketone (VIII) in 6 ml of benzene was poured into an aluminum oxide column containing 2% of potassium hydroxide, left for 2 hr, and the product eluted with benzene and dioxane. After three crystallizations from aqueous methanol there was obtained 80 mg of diketone (IX), m. p. 158.5-159.5°;  $\nu$  (in CHCl<sub>3</sub>) 1719 cm<sup>-1</sup> (K 2680). Found: C 73.17, 73.36; H 7.97, 7.95%. C<sub>21</sub>H<sub>28</sub>O<sub>4</sub>. Calculated: C 73.22; H 8.19%. A sample, mixed with the above-described diketone (VIIIa), melted at 136-144°.

DL-18-nor-D-homo-3,15,17-triacetoxy- $\Delta^{9(11)}$ -androstenes (Xa, b). A solution of 0.1 g of diketone (IX) in 20 ml of alcohol and 5 ml of dioxane was reduced with 40 mg of sodium borohydride. The resulting product was acetylated; after chromatographing on aluminum oxide and elution with benzene, triacetate (Xa), m. p. 160-161° (from aqueous methanol), was obtained. On elution with ether the isomeric triacetate (Xb), m. p. 194-195° (from aqueous methanol), was isolated. Both triacetates (X) give no melting-point depression with known samples described earlier.

#### SUMMARY

18-nor-14-iso- $\Delta^{9(11)}$ -Androstene-15,17-dione derivatives (V) and (VI) were prepared on the basis of the diene condensation of trans-1-vinyl-6-acetoxy- and trans-1-vinyl-6-ethylenedioxy-9-methyl- $\Delta^9$ -octalins with cyclopentenone-1,3.



#### LITERATURE CITED

1. I. A. Gurvich, T. V. Ilyukhina, and V. F. Kucherov, *Izv. AN SSSR, Otd. Khim. Nauk* 1960, 1706.
2. V. F. Kucherov and L. N. Ivanova, *Doklady AN SSSR* 131, No. 5, 1077 (1960).
3. I. N. Nazarov and I. A. Gurvich, *Izv. AN SSSR, Otd. Khim. Nauk* 1959, 293.

---

All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

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# TEMPERATURE COEFFICIENT OF RADIOCHEMICAL REACTIONS AND ITS CONNECTION WITH PRIMARY WATER-RADIOLYSIS PROCESSES

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Processes, occurring in the radiolysis of aqueous solutions, have been explained by resorting to concepts of hydrogen bonds through which energy can be transmitted in water for considerable distances to any ion or molecule [1, 2]. Since temperature affects the structure of water (see, e.g. [3]), it is to be expected that as the temperature rises, the efficiency of energy transmission through the hydrogen-bond system should decrease, and hence the temperature coefficient of radiochemical nonchain reactions in sufficiently-dilute aqueous solutions, should be negative. Data on the temperature dependence of the well-known radiochemical reactions of  $\text{Fe}^{2+}$  oxidation and  $\text{Ce}^{4+}$  reduction, are given in the table.

Temperature Dependence of Radiochemical Reactions

Solution composition	Type of radiation	Investigated temperature interval, °C	Temperature coefficient in % per 1°	Apparent activation energy, cal	Literature
$\text{Ce}(\text{SO}_4)_2$	Ra $\gamma$ -rays	20-90		-370	
in 0.8 $\text{NH}_2\text{SO}_4$				-650	[4]
$\sim 1.2 \cdot 10^{-4} \text{M Ce}(\text{NH}_4)_2 \cdot (\text{SO}_4)_3$ in 0.8 $\text{NH}_2\text{SO}_4$		5.8-73		-300	[5]
0.03 M $\text{Ce}(\text{SO}_4)_2$		7-61		-620	[6]
$10^{-3}$ M $\text{FeSO}_4$ and $10^{-3}$ M NaCl in 0.8 N $\text{H}_2\text{SO}_4$	$\text{Co}^{60}$ $\gamma$ -rays	4-54.5	$+0.04 \pm 0.03$		[7]
$10^{-3}$ M $\text{FeSO}_4$	$\text{Co}^{60}$ $\gamma$ -rays	31-60	+0.2	$+550 \pm 50$	[8]
in 0.8 $\text{NH}_2\text{SO}_4$					
$1.82 \cdot 10^{-3}$ M $\text{FeSO}_4$	Ra $\gamma$ -rays	4-54	0		[9]

The opposite signs of the temperature coefficients of these reactions, are noteworthy. This difference cannot be due to the effect of temperature on the diffusion of water-radiolysis products, since the radiochemical yields of  $G(\text{Fe}^{3+}) = 3\text{C}_\text{H} + 2\text{C}_{\text{H}_2\text{O}_2} + \text{GOH}$  and  $G(\text{Ce}^{3+}) = \text{G}_\text{H} + 2\text{G}_{\text{H}_2\text{O}_2} - \text{GOH}$  are determined by reactions of the same radiolysis products. The observed difference apparently is due to a difference in the groupings surrounding the corresponding ions of variable valence in the solutions under investigation. In solutions of ceric sulfate in 0.8 N  $\text{H}_2\text{SO}_4$ ,  $\text{Ce}^{4+}$  ions are not hydrated, and occur mainly in the form of  $\text{Ce}(\text{SO}_4)_3^{2-}$  ions not containing hydrogen or hydroxyl ions [10]. In acid solutions of ferrous sulfate  $\text{Fe}^{2+}$  ions, as is well known, are surrounded by a hydration shell. Therefore, despite the fact that as the temperature rises in both reaction systems, the efficiency of energy transmission through the hydrogen bonds decreases, the positive temperature coefficient of the  $\text{Fe}^{2+}$ -oxidation process as a whole is due to the predominant role of reactions in the hydration shell of the  $\text{Fe}^{2+}$  ion, having a positive temperature coefficient.

Thus investigation of the temperature dependence of a number of radiochemical nonchain reactions and comparison of their temperature coefficients may give direct information both on the process of energy transmission through intermolecular bonds and on reactions taking place in the immediate vicinity of the cation of variable valence. It is interesting to note that when the temperature dependence of  $G(\text{Ce}^{3+})$  is plotted, according to data of [5, 6], in  $\log G - 1/T$  coordinates in both cases, despite the considerable dispersion of the experimental data, a region

is clearly visible, in which  $G(\text{Ce}^{3+})$  is practically independent of the temperature if the latter does not exceed  $27^\circ$ . This possibly is due to the persistence of a considerable proportion of hydrogen bonds in aqueous solutions in the given temperature range [3].

#### SUMMARY

1. A hypothesis on the negative temperature coefficient of radiochemical nonchain reactions in dilute aqueous solutions, is advanced.

2. The temperature coefficients of the radiochemical reactions of  $\text{Ce}^{4+}$  reduction and  $\text{Fe}^{2+}$  oxidation, are compared. The positive temperature coefficient for the latter reaction apparently is due to the positive temperature coefficients of reactions in the hydration shell of the ion.

#### LITERATURE CITED

1. G. von Büнау, K. C. Kurien, W. H. Taylor, and L. M. Theard, Summary of Proceedings of an Informal Discussion of the Radiation Chemistry of Water. Radiation Project, University of Notre Dame, Jan. 8-9, 1959; M. Burton, J. Chem. Educ. 36, 277 (1959).
2. V. V. Voevodskii, Abstracts of Proceedings of the 11th All-Union Conference on Radiochemistry [in Russian] (Moscow, Acad. Sci. USSR Press, 1960) p. 25.
3. F. S. Feates and D. J. G. Ives, J. Chem. Soc. 1956, 549.
4. H. Hotta and K. Shimada, Bull. Chem. Soc. Japan 33, 114 (1960).
5. T. J. Hardwick, Canad. J. Chem. 30, 23 (1952).
6. S. J. Taimuty, L. H. Towle, and D. L. Peterson, Nucleonics 17, N 8, 103 (1959).
7. H. A. Schwarz, J. Amer. Chem. Soc. 76, 1587 (1954).
8. T. J. Hardwick, Canad. J. Chem. 31, 881 (1953).
9. W. Minder and A. Liechti, Experientia 2, 410 (1946).
10. T. J. Hardwick and E. Robertson, Canad. J. Chem. 29, 828 (1951).

---

All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. Some or all of this periodical literature may well be available in English translation. A complete list of the cover-to-cover English translations appears at the back of this issue.

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# SYNTHESIS OF o-HYDROXYBENZENESULFINIC ACID - A NEW ANALYTICAL REAGENT

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Translated from *Izvestiya Akademii Nauk SSSR, Otdeleniye Khimicheskikh Nauk*,

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As we noted earlier [1, 2], sulfinic acids are similar in many ways to carboxylic acids in their chemical behavior toward metal ions. In connection with this a successful attempt was made to synthesize and to study o-hydroxybenzenesulfinic acid, which is a structural analog of salicylic acid; the sulfo derivative of the latter is widely used in analytical practice. The chemical properties of the new reagent and its advantages over salicylic acid were described in the above-mentioned article [1], but its synthesis was not published.

o-Hydroxybenzenesulfinic acid was prepared by us for the first time on the basis of the general principal of sulfinic acid synthesis by Gattermann method [3], including the Sandmeyer reaction. This method was improved and modified in accordance with the properties of the product, since methods of extraction of sulfinic acids in general, and their purification in particular, have scarcely been described in the literature.

## EXPERIMENTAL

Ten g of o-aminophenol was dissolved in a mixture of 5 ml of concentrated sulfuric acid and 100 ml of water. This solution was filtered, and diazotized by alternate, dropwise addition from separatory funnels of an ice-cooled mixture of 25 ml of concentrated sulfuric acid and 10 ml of water and a solution of 8 g of  $\text{NaNO}_2$  in 25 ml of water, which was stopped when the reaction was finished, as shown by starch-iodide paper.

The diazonium salt solution was added dropwise to a mixture of 70 g of copper powder and 100 ml of saturated sodium sulfite solution containing the solid phase of this salt (10-15 g). At first the reacting mixture turned red; at the end of the reaction the solution over the precipitate became green. The product formed was distributed between the solid and liquid phases. The solid phase was filtered out, and shaken several times with 50 ml portions of ether; the ethereal extracts were collected. Then the filtrate, left after removal of the solid phase, was extracted with similar portions. These ethereal extracts also were collected, and added to the ethereal extracts of the solid phase. The combined extract was filtered, and left to stand until its volume was decreased by evaporation to 200-250 ml. After this the solution, together with anhydrous sodium sulfate, was placed in a jar with ground glass stopper for 2 days, and then the ether was evaporated in air until prismatic crystals appeared in the residue. These crystals were filtered out with a glass filter and recrystallized two or three times from absolute ether. Yield 2.5-3 g of product. Found: S 19.98, 20.03%.  $\text{C}_6\text{H}_6\text{SO}_3$ . Calculated: S 20.27%.

o-Hydroxybenzenesulfinic acid (mol. wt. 158, 174) consists of colorless, prismatic crystals (m. p.  $71^\circ$ ) very soluble in water, ether, alcohol, and acetone. Contrary to salicylic acid, this substance sublimes with difficulty (only in vacuo); it fluoresces weakly in ultraviolet light; with concentrated sulfuric acid it forms a blue coloration (qualitative reaction for the sulfinic group), whereas a red color appears on addition of  $\text{Ti}^{4+}$  to this solution (qualitative reaction for the enol group) [4]. On prolonged standing in air and in solution o-hydroxybenzenesulfinic acid, like all sulfinic acids, decomposes [4]; moreover, it can be oxidized by strong oxidizing agents and reduced by strong reducing agents. No doubt its alkali and ammonium salts will be sufficiently stable in solution and especially in the dry state.

o-Hydroxybenzenesulfinic acid forms precipitates with quadrivalent cations, as well as scandium, bismuth, and lead. Moreover, this acid forms soluble, colored complexes with  $\text{Fe}^{\text{III}}$ ,  $\text{U}^{\text{VI}}$ ,  $\text{Co}^{\text{II}}$ ,  $\text{Ni}^{\text{II}}$  and  $\text{Cu}^{\text{II}}$ . This reagent enters into the main chemical reactions characteristic of salicylic acid.



## SUMMARY

A new analytical reagent has been synthesized — o-hydroxybenzenesulfinic acid; this is confirmed by its chemical behavior, analysis for its sulfur content, and also qualitative reactions for analytical functional groups.

## LITERATURE CITED

1. I. P. Alimarin and D. I. Kuznetsov, Dokl. AN SSSR 131, No. 4, 821 (1960).
2. D. I. Kuznetsov, Dissertation, Moscow State Univ., Moscow, 1960.
3. L. Gattermann, Ber. 32, 1136 (1899).
4. I. P. Alimarin and D. I. Kuznetsov, Vestn. Mosk. Univ. seriya mat., mekh., astr., fiz. i khim. nauk No. 3, 189 (1959).

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

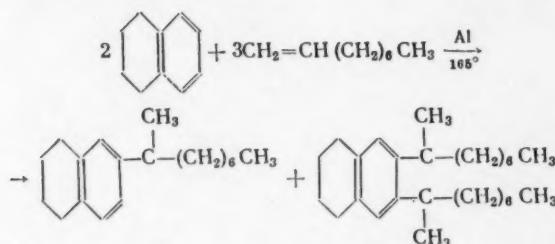
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# CATALYTIC ALKYLATION OF TETRALIN BY NONENE-1 IN THE PRESENCE OF ALUMINUM

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Original article submitted December 14, 1960

In our preceding articles [1-3] it was shown that the alkylation of tetralin by alkenes takes place only at elevated pressure. In the presence of  $ZnCl_2$  on  $Al_2O_3$ ,  $Al_2O_3 \cdot SiO_2$ , or  $ZnCl_2$ , the yield of alkyltetralins did not exceed 25%, reckoned on initial tetralin, or 48%, reckoned on initial alkenes. The yield, reckoned on reacted tetralin, reached 70%. In the present work the possibility of alkylating tetralin with alkenes at atmospheric pressure is shown in the case of alkylation of tetralin by nonene-1.



The experiments were performed in a flask with a mechanical stirrer in the presence of metallic aluminum, which was highly recommended for benzene alkylation [4-6]. The alkylation of tetralin by nonene-1 was carried out in *n*-nonane solution. Nonyl bromide was used to activate the aluminum. Freshly-prepared aluminum filings (0.01 mole) were added to a mixture of 0.25 mole of tetralin, 0.03 or 0.06 mole of nonyl bromide, and 20 ml of nonane. The mixture was first boiled ( $\sim 170^\circ$ ) until the reaction began, at which time the reaction mass turned brown and evolved hydrogen bromide. After this the mixture was brought to the required temperature, 24 g of nonene-1 was introduced dropwise, and 40 ml of nonane was then added. The reaction mass was heated at the specified temperature for 1-4 hr. On cooling, the reaction product was decomposed by water acidified with hydrochloric acid, and after the usual treatment was distilled in a column with an efficiency of 20 theoretical plates. In this case nonane-nonene, tetralin, and nonyltetralin fractions were taken. Results of typical experiments are given in Table 1.

TABLE 1. Results of Alkylation of Tetralin by Nonene-1 in the Presence of Aluminum

Initial nonyl bromide, moles	Temperature, $^\circ C$	Duration of experiment, hr	Yield of nonyltetralin fractions		
			b.p. 190-200° (9 mm)		b.p. 200-230° (9 mm)
			g	% of theoret.	
0,03	140	3	26,0	40,5	10,0
0,03	165	1	35,1	54,4	9,5
0,03	165	2	35,0	54,4	10,5
0,06	165	2	35,0	54,4	15,8
0,06	165	3	32,3	49,7	10,0
0,06	165	4	32,0	40,6	10,1
0,06	185	2	35,1	54,4	14,5

From the data of Table 1 it is evident that in the alkylation of tetralin by nonene-1 in the presence of 0.01 mole of aluminum, 0.03 mole of nonyl bromide is sufficient for its activation. At 165° nonene-1 reacts completely with tetralin within 2 hr to form nonyl- and dinonyltetralins. The yield of crude nonyltetralin was 54.4% of theoretical, reckoned on the initial components, and 81.5%, reckoned on reacted tetralin.

In order to determine the structure of the nonyltetralins we isolated the narrow fractions: I - b. p. 190° (7 mm);  $n_D^{20}$  1.5120;  $d_4^{20}$  0.9117; II - b.p. 190-191° (7 mm);  $n_D^{20}$  1.5130;  $d_4^{20}$  0.9170. Found MR 84.53; 84.33.  $C_{19}H_{33}$ . Calculated MR 84.14; III - b.p. 215-220° (6 mm);  $n_D^{20}$  1.5130;  $d_4^{20}$  0.9113. Found MR 126.2.  $C_{23}H_{38}$ . Calculated MR 125.7.

These fractions were investigated by means of their IR spectra.\* The IR spectra were taken with an IKS-12 instrument in the 700-900, 1600-2000, and 2800-3000  $cm^{-1}$  regions. In the spectra of fractions I and II were found the 720, 725, 750w, 810s, 830s, 1612, 1750s, 1850, 1885s, and 2000  $cm^{-1}$  bands, which are characteristic of alkyltetralins substituted in position 6. In the spectrum of fraction III (b. p. 215-220°) the 727, 750, 828, 870, 1600, 1730s, 1890, and 2000w  $cm^{-1}$  bands were found. The spectrum of this fraction coincides with that of 6,7-di-n-hexyltetralin (spectrum in the Spectroscopy Commission, Academy of Sciences, USSR). In the 2800-3000  $cm^{-1}$  region the absorption coefficients  $\epsilon_1$  and  $\epsilon_2$  were determined for the 2926 and 2956  $cm^{-1}$  bands, and the numbers of  $CH_2$  and  $CH_3$  groups [7], given in Table 2, were calculated there from.

TABLE 2. Results of Spectral Investigations of Nonyl- and Dinonyltetralin Fractions in the 2800-2000  $cm^{-1}$  Region

Fraction number	Number of $CH_2$ group	$\epsilon_1$	Number of $CH_3$ group	$\epsilon_2$	Structural formula
I	9,2	570	2	203	
II	9,5	590	1,9	187	
III	16,0	895	3,7	350	

\*The IR spectra were taken by E. D. Lubuzh, for which the authors express their thanks.

#### SUMMARY

Isononyl- and dinonyltetralins are formed in the alkylation of tetralin by nonene-1 in the presence of metallic aluminum activated by nonyl bromide.

#### LITERATURE CITED

1. N. I. Shulkin and N. A. Pozdnyak, *Izv. AN SSSR, Otd. Khim. Nauk* **1960**, 1094.
2. N. I. Shulkin, N. A. Pozdnyak, and V. A. Shlyapochnikov, *Izv. AN SSSR, Otd. Khim. Nauk* **1960**, 1254.
3. N. I. Shulkin and N. A. Pozdnyak, *Izv. AN SSSR, Otd. Khim. Nauk* **1960**, 1094.
4. V. D. Azatyan, *Dokl. AN SSSR* **59**, 901 (1948).
5. N. G. Sidorova, I. P. Tsukervanik, and Z. Abidova, *Dokl. AN Uz.SSR* **5**, 33 (1953).
6. N. G. Sidorova, I. P. Tsukervanik, and E. Pak, *Zh. obshch. khimii* **24**, 94 (1954).
7. N. I. Shulkin, V. A. Shlyapochnikov, N. A. Pozdnyak, and B. L. Lebedev, *Izv. AN SSSR, Otd. Khim. Nauk* **1961**, 466.

# ON THE ACTION OF AMINES AND AMMONIA ON TRIALLYLBORON

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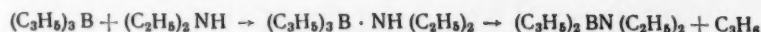
Translated from *Izvestiya Akademii Nauk SSSR, Otdeleniye Khimicheskikh Nauk*,

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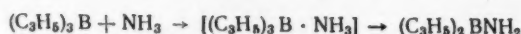
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Triallylboron is highly reactive toward reagents with mobile hydrogen; contrary to trialkylborons [1], it reacts with water, alcohols [2], and mercaptans [3] at room temperature; depending on the nature of the nucleophilic reagent and the ratio of the original substances, one or two allyl radicals are split off, and the corresponding diallyl or monoallyl boron compounds are formed. The increased reactivity of triallylboron is explained by the hypothesis, that the energy of the bonds between the allyl radicals and the boron atom is much lower than that of alkyl-boron bonds, which is based on comparison of the energies of bonds between allyl and alkyls and various other atoms [4]. As we found earlier [2], the reaction of triallylboron with n-butylamine requires a higher temperature than its reactions with water, alcohols, or mercaptans; however, the process goes much more readily than with trialkylborons [3].

In order to find out the effect of the nature of the amines on the ease with which they react with triallylboron, we investigated its transformations on treatment with ethylamine, diethylamine, aniline, and ammonia. In the first stage of the reaction of triallylboron with amines, complex compounds are formed. Thus in the reaction of triallylboron and diethylamine heat is evolved and a complex (1) is formed, which splits off propylene at 100-130°, being converted to diallyl(diethylamino)boron in 93% yield.



The reaction of triallylboron with ethylamine goes similarly, giving diallyl(ethylamino)boron as a final product. Triallylboron reacts more vigorously with aniline, evolving propylene on mixing of the reagents and being converted to diallyl(phenylamino)boron in 77.5% yield. With ammonia triallylboron forms a complex compound which on distillation gives a moderate yield of diallyl(amino)boron.



## EXPERIMENTAL

All operations were carried out in a nitrogen atmosphere.

**Diethylamine-triallylboron.** To 6.9 g (0.0515 mole) of triallylboron, 4.1 g (0.056 mole) of diethylamine was slowly added dropwise, the mixture being stirred and cooled so that the temperature within the reaction mass was 30-35°. Then the reaction mixture, cooled to 0°, was kept in vacuo (10 mm) for 10 min. There was obtained 10.3 g (96.7%) of the triallylboron-diethylamine complex;  $d_4^{20}$  0.8397;  $n_D^{20}$  1.4812. Found: C 74.60; H 12.89; B 4.08%.  $\text{C}_{13}\text{H}_{26}\text{BN}$ . Calculated: C 75.37; H 12.65; B 5.22%.

**Diallyl(diethylamino)boron.** When 8.4 g (0.405 mole) of the triallylboron-diethylamine complex was heated at 100-130°, 0.035 mole of propylene was evolved. The liquid was distilled in vacuo. There was obtained 6.2 g (92.6%) of diallyl(diethylamino)boron, b. p. 69-72° (11 mm). After redistillation diallyl(diethylamino)boron had b. p. 79-80° (20 mm);  $d_4^{20}$  0.8025;  $n_D^{20}$  1.4562. Found: C 72.98, 72.69; H 12.07, 12.06; B 6.77, 6.7%.  $\text{C}_{10}\text{H}_{20}\text{BN}$ . Calculated: C 72.75; H 12.21; B 6.55%. The substance fumed in air and dissolved in organic solvents. Diallyl(diethylamino)boron could be prepared, without isolating the complex, by adding the amine to the triallylboron and then distilling the reaction mixture.

**Diallyl(ethylamino)boron.** To 5.7 g (0.042 mole) of triallylboron, 2.7 g (0.059 mole) of ethylamine was added with stirring; the reaction mixture became quite warm, but no gas was evolved. When all the ethylamine had been added, the mixture was heated for 1 hr at 100-110°; in this case 0.035 mole of propylene was obtained.



On distillation 4.9 g (85.2%) of diallyl(ethylamino)boron, b. p. 76-80° (51 mm), was isolated. On redistillation the substance had b. p. 63-64.5° (26 mm);  $d_4^{20}$  0.8394;  $n_D^{20}$  1.4686; b. p. 14-17°; it fumed in air. Found: C 69.62, 69.63; H 11.55, 11.68; B 8.29, 8.07%.  $C_8H_{16}BN$ . Calculated: C 70.11; H 11.77; B 7.90%.

Diallyl(phenylamino)boron. To 9.3 g (0.0696 mole) of triallylboron, 6.5 g (0.0696 mole) of aniline was added dropwise with stirring; the mixture became quite warm. Gas was vigorously evolved even on addition of the first drops of the amine. In this experiment 0.058 mole of propylene was obtained. On distillation of the liquid reaction products 9.9 g (77.4%) of diallyl(phenylamino)boron, b. p. 77-78° (2 mm), was isolated;  $d_4^{20}$  0.9215;  $n_D^{20}$  1.5342. Found: C 78.09, 78.26; H 8.52, 8.55; B 6.41, 6.16%.  $C_{12}H_{16}BN$ . Calculated: C 77.87; H 8.71; B 5.84%.

Diallyl(amino)boron. A current of dry ammonia was passed into triallylboron (8 g, 0.0597 mole) for 30 min, the temperature of the spontaneously-heating reaction mass being kept at about 60° by external water-cooling. On distillation of the solidified reaction mixture there was obtained 3.2 g (49.3%) of diallyl(amino)boron, b. p. 50-62° (18 mm). On redistillation diallyl(amino)boron had b. p. 58-60° (23 mm);  $d_4^{20}$  0.8686;  $n_D^{20}$  1.4902. Found: C 66.13, 66.27; H 10.79, 10.99; B 9.93, 9.97%.  $C_6H_{12}BN$ . Calculated: C 66.12; H 11.10; B 9.93%. The residue in the distilling flask (1.1 g) was a solid mass.

#### SUMMARY

On treatment of triallylboron with ammonia or amines, diallyl(amino)boron or N-substituted derivatives thereof are formed.

#### LITERATURE CITED

1. B. M. Mikhailov, Yu. N. Bubnov, and V. A. Vaver, Dokl. AN SSSR 126, 575 (1959).
2. B. M. Mikhailov and F. B. Tutorskaya, Dokl. AN SSSR 123 (1958).
3. B. M. Mikhailov and F. B. Tutorskaya, Izv. AN SSSR, Otd. Khim. Nauk 1960, 2068.
4. T. Cottrell, Strength of Chemical Bonds [Russian translation] (Moscow, IL, 1956).

---

All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. Some or all of this periodical literature may well be available in English translation. A complete list of the cover-to-cover English translations appears at the back of this issue.

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# A NEW METHOD OF VITAMIN A SYNTHESIS

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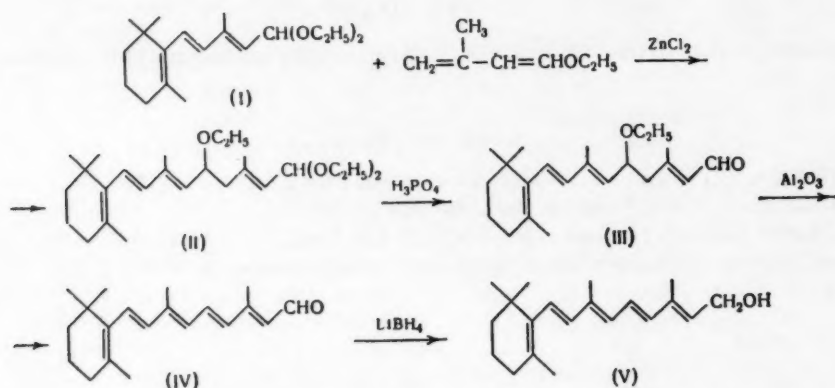
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On the basis of the general method of building up isoprenoid chains through the condensation of unsaturated-aldehyde acetals with 1-ethoxysiprene, which we developed earlier [1], a new, simple way to synthesize vitamin A, according to the following scheme, has been worked out.



The  $\beta$ -ionolideacetaldehyde acetal (I), required for this, was formed in high yield in the reaction of orthoformic ester with  $\beta$ -ionolideacetaldehyde which in turn was obtained in 75% (reckoned on the initial 1-ionone) by the Arens-van Dorp method [2], improved by us.

The condensation of acetal (I) with ethoxysiprene goes smoothly in the presence of zinc chloride, giving ethoxyaldehyde acetal (II) in 62% yield; the latter may be quantitatively hydrolyzed by orthophosphoric acid to vitamin A ethoxyaldehyde (III). Alkoxy groups in  $\delta$ -alkoxyaldehydes are usually split out by heating in the presence of acids [3], which cannot always be used for complex polyene systems. We found that, in the case of ethoxyaldehyde (III) this reaction readily occurs when the latter is chromatographed on alumina, and leads to a satisfactory yield of vitamin A aldehyde (IV). We obtained vitamin A aldehyde by this method in the form of a 50% concentrate which gave an intense Carr-Price reaction and had the 380 m $\mu$  absorption maximum characteristic of retinene. Reduction of this concentrate with lithium borohydride gave an oil which, according to its UV spectrum ( $\lambda_{\text{max}}^{\text{C}_2\text{H}_5\text{OH}}$  324.5 m $\mu$ ;  $\epsilon$  23000), contained more than 50% vitamin A (V). The melting point and UV spectrum of the crystalline  $\beta$ -anthraquinonecarboxylic ester obtained from it were the same as for the corresponding ester of natural vitamin A [4].

## EXPERIMENTAL

$\beta$ -Ionolideacetaldehyde diethyl acetal (I). A mixture of 30 g of  $\beta$ -ionolideacetaldehyde, 31 ml of ethyl orthoformate, 12 ml of absolute ethanol, and 10 mg of p-toluenesulfonic acid was left for three days at room temperature. Then the reaction mass was neutralized with ethanolic sodium ethoxide solution, diluted with ether, and washed with sodium bicarbonate solution and water. The ethereal solution was dried with anhydrous potash and distilled in vacuo. There was obtained 33.5 g (yield 83%) of  $\beta$ -ionolideacetaldehyde acetal (I), b. p. 101-104° (0.06 mm);  $n_D^{20}$  1.5165. Found: C 78.33, 78.49; H 10.60, 10.90%.  $\text{C}_{19}\text{H}_{32}\text{O}_2$ . Calculated: C 78.02; H 11.03%.

**Vitamin A ethoxyaldehyde acetal (II).** To a mixture of 47.5 g of  $\beta$ -ionolideneacetaldehyde acetal (I) and 6 ml of a 10% solution of zinc chloride in ethyl acetate, 9 g of ethoxyisoprene was added, with stirring, during 1 hr; in this case the reaction-mass temperature rose from 23 to 32°. Then the mixture was stirred for 45 min at room temperature and 15 min at 40°, after which the reaction mass was cooled, diluted with absolute ether, washed with 5% sodium hydroxide solution and water, dried with anhydrous potash, and distilled: fr. I, b. p. 98-100° (0.25 mm),  $n_D^{20}$  1.5180; 25.7 g (original acetal I); fr. II, b. p. 157-161° (0.25 mm), 157-161° (0.25 mm);  $n_D^{20}$  1.5140; 19.8 g. Fraction II (a thick, yellow oil) was vitamin A ethoxyaldehyde acetal (II), and its yield was 62%, reckoned on ethoxyisoprene. Found: C 77.72, 77.77; H 10.85, 10.81%.  $C_{26}H_{44}O_3$ . Calculated: C 77.20; H 10.96%.

**Vitamin A ethoxyaldehyde (III).** A mixture of 23 g of vitamin A ethoxyaldehyde acetal (II), 59 ml of 5% orthophosphoric acid, and 12.5 ml of ethanol was boiled in a current of nitrogen, with stirring, for 1 hr. After cooling, the mixture was diluted with ether, washed with sodium bicarbonate solution and water, dried with anhydrous magnesium sulfate, and distilled. There was obtained 16.8 g (90% yield) of vitamin A ethoxyaldehyde (III) in the form of a thick, yellow oil with b. p. 138-140° (0.07 mm);  $n_D^{20}$  1.5377;  $\lambda_{max}$  ( $C_2H_5OH$ ) 241.5 m $\mu$ ,  $\epsilon$  18070; 276 m $\mu$ ,  $\epsilon$  15210; 332 m $\mu$ ,  $\epsilon$  2480. Found: C 79.73, 79.61; H 10.60, 10.59%.  $C_{22}H_{34}O_2$ . Calculated: C 79.95; H 10.37%.

**Vitamin A aldehyde (IV).** A 6.3 g quantity of ethoxyaldehyde (III), dissolved in petroleum ether (b. p. 40-60°) was put into a column (d = 3 cm) containing 300 g of alumina of the third level of activity according to Brockman. On elution with petroleum ether (2300 ml) there was obtained 2.15 g of a faintly-colored substance with  $n_D^{20}$  1.5285, which after distillation had b. p. 130-132° (0.08 mm);  $n_D^{20}$  1.5302;  $\lambda_{max}$  ( $C_2H_5OH$ ) 244.5 m $\mu$ ,  $\epsilon$  15900; 276 m $\mu$ ,  $\epsilon$  13310. Found: C 79.73, 79.58; H 10.25, 10.49%.  $C_{22}H_{34}O_2$ . Calculated: C 79.95; H 10.37%. The isolated product did not change when it was rechromatographed on alumina; in its elementary analysis and UV spectrum it corresponded to the original ethoxyaldehyde (III), and apparently was its geometrical isomer.

On elution with 1100 ml of a petroleum ether-benzene mixture (3:1) there was obtained 1.8 g of a thick, red oil which gave the bright-blue color with  $SbCl_5$  in chloroform, characteristic of vitamin A aldehyde (Carr-Price reaction);  $\lambda_{max}$  ( $C_2H_5OH$ ) 380 m $\mu$ ,  $\epsilon$  25700. According to the ultraviolet absorption intensity the oil obtained was a 60% concentrate of vitamin A aldehyde. Further elution with ether gave a dark-red oil ( $\lambda_{max}$   $C_2H_5OH$  300 m $\mu$ ,  $\epsilon$  13400) apparently consisting of conversion by-products.

**Vitamin A (V).** To 70 mg of lithium borohydride in 25 ml of absolute ether, 0.45 g of the vitamin A aldehyde (IV) concentrate, prepared above, in 20 ml of absolute ether was added during 1 hr, after which the reaction mixture was stirred for 2 hr at room temperature, then cooled with ice water, and 10 ml of 10% potassium hydroxide solution added. The ethereal solution was washed several times with water and dried with anhydrous sodium sulfate. After evaporating the ether in vacuo at room temperature there was obtained 0.4 g of a thick, yellow oil which gave an intense, blue color with  $SbCl_5$  in chloroform;  $\lambda_{max}$  ( $C_2H_5OH$ ) 324 m $\mu$ ;  $E_{1\%}^{1cm}$  804. The  $\beta$ -anthraquinone-carboxylic ester, obtained from it, had m. p. 119-121° after four crystallizations from acetone;  $\lambda_{max}$  ( $C_2H_5OH$ ) 257, 329 m $\mu$ . According to literature data [4, 5] crystalline vitamin A has  $\lambda_{max}$  ( $C_2H_5OH$ ) 325 m $\mu$ ;  $E_{1\%}^{1cm}$  1720; whereas its  $\beta$ -anthraquinonecarboxylic acid ester melts at 122° [ $\lambda_{max}$  ( $C_2H_5OH$ ) 328 and 225 m $\mu$ ].

#### SUMMARY

A new way to synthesize vitamin A, based on the condensation of  $\beta$ -ionolideneacetaldehyde acetal with ethoxyisoprene, is proposed.

#### LITERATURE CITED

1. I. N. Nazarov and Zh. A. Krasnaya, Dokl. AN SSSR **118**, 716 (1958).
2. J. F. Arens and D. A. van Dorp, Recueil trav. chim. **76**, 973 (1948).
3. I. N. Nazarov and Zh. A. Krasnaya, Zh. obshch. khimii **28**, 2440 (1958); Dokl. AN SSSR **121**, 1034 (1958).
4. C. D. Robeson and J. C. Baxter, J. Amer. Chem. Soc. **69**, 140 (1947).
5. O. Isler, W. Huber, A. Roneo, and M. Kofler, Helv. chim. acta **30**, 1911 (1947).

# LETTERS TO THE EDITOR

## SYNTHESIS OF $\Delta^{4,9}$ -D-HOMOESTRADIENOL-14 $\xi$ -DIONE-3,17a

N. N. Gaidamovich and I. V. Torgov

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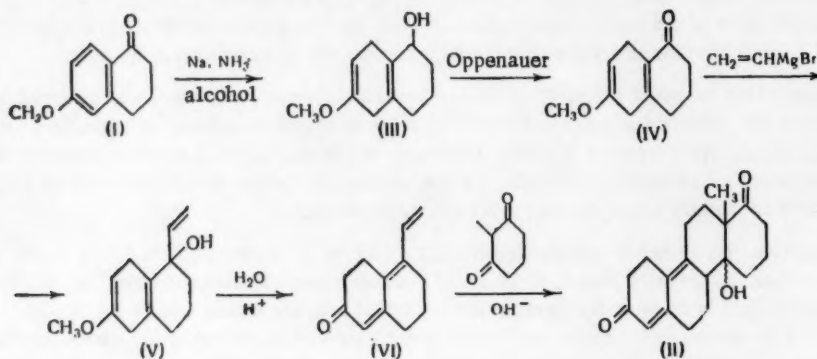
Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*,

No. 6, p. 1162, June, 1961

Original article submitted March 20, 1961

Proceeding from the available 6-methoxytetralone (I), we synthesized  $\Delta^{4,9}$ -D-homoestradienol-14 $\xi$ -dione-3,17a (II) — an interesting example of steroid compounds with angular hydroxyl.

6-Methoxytetralone (I) was reduced by the Birch method [1] to carbinol (III) [yield 77%, m. p. 73-74°;  $\lambda_{\max}$  (in alcohol) 276 m $\mu$ ;  $\log \epsilon$  2.23], which in turn was converted by Oppenauer oxidation to 6-methoxy- $\Delta^{6,9}$ -hexalone (IV) [yield 94%, m. p. 45-47°;  $\lambda_{\max}$  (alcohol) 239 m $\mu$ ;  $\log \epsilon$  3.98]. Condensation of ketone (IV) with vinylmagnesium bromide led to carbinol (V), which after hydrolysis gave the unstable 1-vinyl- $\Delta^{1(9),5(10)}$ -hexalone-6 (VI) [ $n_D^{20}$  1.6304;  $\lambda_{\max}$  (in alcohol) 226, 321 m $\mu$ ;  $\log \epsilon$  4.01, 4.32].



Condensation of trienone (VI) with methylidihydroresorcinol in the presence of diethylamine gave hydroxy-diketone (II) [yield 25%, m. p. 207-209;  $\lambda_{\max}$  (in alcohol) 306 m $\mu$ ,  $\log \epsilon$  4.43; 1703, 1639, 1613, 1580, 3450 cm<sup>-1</sup>].

### LITERATURE CITED

1. A. J. Birch, I. A. K. Quartey, and H. Smith, *J. Chem. Soc.* **1952**, 1769.



## POLYMERS AND TRIMERS OF ALKYL MERCAPTOBORANES

B. M. Mikhailov, T. A. Shchegoleva, E. M. Shashkova,  
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Translated from *Izvestiya Akademii Nauk SSSR, Otdeleniye Khimicheskikh Nauk*,  
No. 6, p. 1163, June, 1961  
Original article submitted April, 20, 1961

We found that the interaction of diborane with mercaptans, taken in the ratio 1:2, in an ether medium gives polymeric alkylmercaptoboranes.

Diborane reacts with methyl mercaptan to form the solid polymer  $(CH_3SBH_2)_x$ , which Burg prepared earlier without using a solvent [1]. On treatment of diborane with ethyl or n-butyl mercaptan, followed by distilling off the ether, vitreous polymers of ethylmercaptoborane,  $(C_2H_5SBH_2)_x$ , or n-butylmercaptoborane,  $(n-C_4H_9SBH_2)_x$ , are obtained. On standing at room temperature polymers of ethylmercaptoborane and n-butylmercaptoborane are converted to the corresponding alkylmercaptoborane trimers. The ethylmercaptoborane trimer has b. p. 94-96° (1 mm);  $d_4^{20}$  0.9772;  $n_D^{20}$  1.5323; Found:  $H_{act}$  2.98, 2.90; B 14.37, 14.27%;  $M^*$  217.8; 220.2.  $(C_2H_5SBH_2)_3$ . Calculated:  $H_{act}$  2.73; B 14.63%;  $M$  221.9. The n-butylmercaptoborane trimer decomposes on distillation in vacuo;  $d_4^{20}$  0.9376;  $n_D^{20}$  1.5130. Found:  $H_{act}$  2.17, 2.15; B 10.23, 10.32%;  $M$  293.3, 294.9.  $(C_4H_9SBH_2)_3$ . Calculated:  $H_{act}$  1.98; B 10.60%;  $M$  306.1.

The solid polymer of methylmercaptoborane is stable on keeping, but on solution in tetrahydrofuran it is converted to the methylmercaptoborane trimer, b. p. 80-81° (1.5 mm);  $d_4^{20}$  1.0121;  $n_D^{20}$  1.5483. Found:  $H_{act}$  3.46, 3.37; B 17.80, 17.30%;  $M$  182.5, 183.6.  $(CH_3SBH_2)_3$ . Calculated:  $H_{act}$  3.34; B 18.10%;  $M$  179.8.

Alkylmercaptoborane trimers have considerable stability toward air and water.

### LITERATURE CITED

1. A. Burg and R. Wagner, *J. Amer. Chem. Soc.*, **76**, 3307 (1954).

\*The molecular weight was found cryoscopically in benzene.

# BIS(ALKYLAMINO)BORANES

B. M. Mikhailov and V. A. Dorokhov

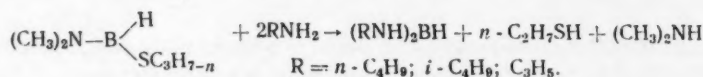
N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR

Translated from *Izvestiya Akademii Nauk SSSR, Otdeleniye Khimicheskikh Nauk*,

No. 6, p. 1163, June, 1961

Original article submitted April 26, 1961

We found that on treatment of n-propylmercapto(dimethylamino)borane with primary amines at 60-70° bis(alkylamino)boranes, hitherto unknown, are obtained in high yields.



n-Propylmercapto(dimethylamino)borane was prepared by treating (dimethylamino)borane with n-propyl mercaptan by the method which we described earlier [1]: b. p. 48-50° (13 mm);  $d_4^{20}$  0.8706;  $n_D^{20}$  1.4701. Found: C 46.43; H 10.64%; M 134.9.  $\text{C}_8\text{H}_{14}\text{NSB}$ . Calculated: C 45.82; H 10.76%; M 131.1.

Bis(n-butylamino)borane had b. p. 46-48° (2 mm);  $d_4^{20}$  0.7879;  $n_D^{20}$  1.4306. Found: C 61.49; H 13.25; B 7.05%; M 147.9.  $\text{C}_8\text{H}_{21}\text{N}_2\text{B}$ . Calculated: C 61.56; H 13.56; B 6.93%; M 156.1. Bis(isobutylamino)borane had b. p. 59-61° (9 mm);  $d_4^{20}$  0.7794;  $n_D^{20}$  1.4263. Found: C 61.26; H 13.33; B 7.23%; M 155.0.  $\text{C}_8\text{H}_{21}\text{N}_2\text{B}$ . Calculated: C 61.56; H 13.56; B 6.93%; M 156.1. Bis(allylamino)borane had b. p. 62-67° (30 mm);  $d_4^{20}$  0.8181;  $n_D^{20}$  1.4520. Found: C 58.31; H 10.38; B 8.92%.  $\text{C}_6\text{H}_{13}\text{N}_2\text{B}$ . Calculated: C 58.12; H 10.52; B 8.73%.

On heating above 150° bis(alkylamino)boranes are converted to N-trialkylborazoles, alkylamines being split off.

## LITERATURE CITED

1. B. M. Mikhailov and V. A. Dorokhov, *Dokl. AN SSSR* **136**, 356 (1961).

All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. Some or all of this periodical literature may well be available in English translation. A complete list of the cover-to-cover English translations appears at the back of this issue.

# SYNTHESIS OF 18-NOR-D-HOMOEQUILENIN METHYL ETHER

A. A. Akhrem, Yu. A. Titov, and I. N. Minaeva

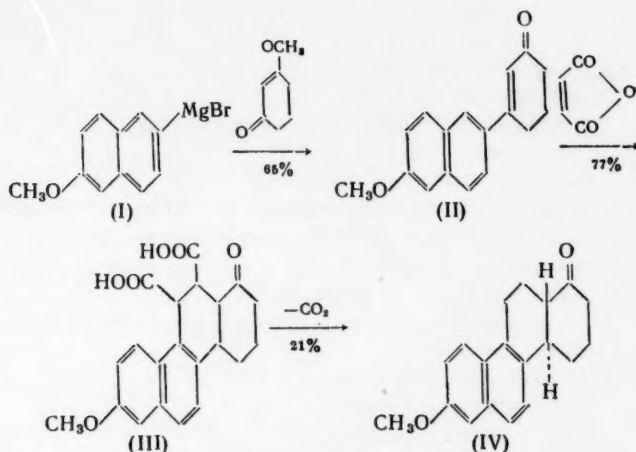
N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR

Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*,

No. 6, p. 1164, June, 1961

Original article submitted May 3, 1961

In the course of investigations of steroid-hormone synthesis we prepared 18-nor-D-homoequilenin methyl ether (IV) according to the scheme:



The Grignard reaction of 6-bromomagnesiumnerolin (I) [1] with dihydroresorcinol methyl ether in a tetrahydrofuran medium led to 3-(6'-methoxy-2'-naphthyl)cyclohexene-2-one-1 (II). The reaction of the latter with a 10-fold excess of maleic anhydride (120°, 30 hr) gave ketodicarboxylic acid (III), m. p. 180-183°; 2,4-dinitrophenylhydrazone, m. p. 142-144°. Found: N 10.12%. C<sub>27</sub>H<sub>24</sub>O<sub>5</sub>N<sub>4</sub>. Calculated: N 10.22%. Decarboxylation of acid (III) in quinoline at 200° in the presence of copper chromite led to (IV), which was identified through the 2,4-dinitrophenylhydrazone, m. p. 243-245° [2]. Found: N 11.94%. C<sub>25</sub>H<sub>24</sub>O<sub>5</sub>N<sub>4</sub>. Calculated: N 12.17%.

## LITERATURE CITED

1. K. Fries and K. Schimmelschmidt, *Ber.* **58**, 2835 (1925).
2. D. Nasipent and J. Roy, *J. Chem. Soc.* **1960**, 1571.

# SIGNIFICANCE OF ABBREVIATIONS MOST FREQUENTLY ENCOUNTERED IN SOVIET PERIODICALS

FIAN	Phys. Inst. Acad. Sci. USSR
GDI	Water Power Inst.
GITI	State Sci. -Tech. Press
GITTL	State Tech. and Theor. Lit. Press
GONTI	State United Sci. -Tech. Press
Gosenergizdat	State Power Press
Goskhimizdat	State Chem. Press
GOST	All-Union State Standard
GTTI	State Tech. and Theor. Lit. Press
IL	Foreign Lit. Press
ISN (Izd. Sov. Nauk)	Soviet Science Press
Izd. AN SSSR	Acad. Sci. USSR Press
Izd. MGU	Moscow State Univ. Press
LEIIZhT	Leningrad Power Inst. of Railroad Engineering
LET	Leningrad Elec. Engr. School
LETI	Leningrad Electrotechnical Inst.
LEIIZhT	Leningrad Electrical Engineering Research Inst. of Railroad Engr.
Mashgiz	State Sci. -Tech. Press for Machine Construction Lit.
MEP	Ministry of Electrical Industry
MES	Ministry of Electrical Power Plants
MESEP	Ministry of Electrical Power Plants and the Electrical Industry
MGU	Moscow State Univ.
MKhTI	Moscow Inst. Chem. Tech.
MOPI	Moscow Regional Pedagogical Inst.
MSP	Ministry of Industrial Construction
NII ZVUKSZAPIOI	Scientific Research Inst. of Sound Recording
NIKFI	Sci. Inst. of Modern Motion Picture Photography
ONTI	United Sci. - Tech. Press
OTI	Division of Technical Information
OTN	Div. Tech. Sci.
Stroiizdat	Construction Press
TOE	Association of Power Engineers
TsKTI	Central Research Inst. for Boilers and Turbines
TsNIEL	Central Scientific Research Elec. Engr. Lab.
TsNIEL-MES	Central Scientific Research Elec. Engr. Lab. - Ministry of Electric Power Plants
TsVTI	Central Office of Economic Information
UF	Ural Branch
VIESKh	All-Union Inst. of Rural Elec. Power Stations
VNIIM	All-Union Scientific Research Inst. of Metrology
VNIIZhDT	All-Union Scientific Research Inst. of Railroad Engineering
VTI	All-Union Thermotech. Inst.
VZEI	All-Union Power Correspondence Inst.

NOTE: Abbreviations not on this list and not explained in the translation have been transliterated, no further information about their significance being available to us. -Publisher.



## Soviet Journals Available in Cover-to-Cover Translation

ABBREVIATION	RUSSIAN TITLE	TITLE OF TRANSLATION	PUBLISHER	TRANSLATION BEGAN
			Vol.	Year
			issue	
AE	Atomnaya energiya	Soviet Journal of Atomic Energy	Consultants Bureau	1956
Akust. zh.	Akusticheskii zhurnal	Soviet Physics - Acoustics	American Institute of Physics	1955
Astr(om). zh(um).	Antibiotiki	Antibiotics	Consultants Bureau	1959
Avto(mat). svarka	Astronomicheskii zhurnal	Soviet Astronomy-AJ	American Institute of Physics	1957
	Avtomatscheskaya svarka	Automatic Welding	British Welding Research Association (London)	1959
	Avtomatika i Telemekhanika	Automation and Remote Control	Instrument Society of America	1956
	Biofizika	Biophysics	National Institutes of Health*	1957
	Biokhimiya	Bulletin of Experimental Biology and Medicine	Consultants Bureau	1956
Byull. eksp(erim). biol. i med.	Byulleten' eksperimental'noi biologii i meditsiny		Consultants Bureau	1957
DAN (SSSR) Doklady AN SSSR }	Doklady Akademii Nauk SSSR	The translation of this journal is published in sections, as follows: Doklady Biochemistry Section Doklady Biological Sciences Sections (Includes: Anatomy, biophysics, cytology, ecology, embryology, endocrinology, evolutionary morphology, genetics, histology, hydrobiology, microbiology, morphology, parasitology, physiology, zoology sections) Doklady Botanical Sciences Sections (Includes: Botany, phytopathology, plant anatomy, plant ecology, plant embryology, plant physiology, plant morphology sections) Proceedings of the Academy of Sciences of the USSR, Section: Chemical Technology Proceedings of the Academy of Sciences of the USSR, Section: Chemistry Proceedings of the Academy of Sciences of the USSR, Section: Physical Chemistry Doklady Earth Sciences Sections (Includes: Geochemistry, geology, geophysics, hydrogeology, mineralogy, paleontology, petrography, permafrost sections) Proceedings of the Academy of Sciences of the USSR, Section: Geochemistry Proceedings of the Academy of Sciences of the USSR, Section: Geology Doklady Soviet Mathematics Soviet Physics-Doklady (Includes: Aerodynamics, astronomy, crystallography, cybernetics and control theory, electrical engineering, energetics, fluid mechanics, heat engineering, hydraulics, mathematical physics, mechanics, physics, technical physics, theory of elasticity sections) Proceedings of the Academy of Sciences of the USSR, Applied Physics Sections (does not include mathematical physics or physics sections) Wood Processing Industry	American Institute of Biological Sciences	1957
		Life Sciences	American Institute of Biological Sciences	1957
		Chemical Sciences	Consultants Bureau	1956
			Consultants Bureau	1956
			Consultants Bureau	1957
		Earth Sciences	American Geological Institute	1959
			Consultants Bureau	1957
			Consultants Bureau	1958
			Consultants Bureau	1957
		Mathematics	Consultants Bureau	1957
			The American Mathematics Society	1961
		Physics	American Institute of Physics	1956
			Consultants Bureau	1956
			Timber Development Association (London)	1957
			Massachusetts Institute of Technology*	1959
			American Institute of Biological Sciences	1959
			Consultants Bureau	1957
			Acta Metallurgica*	1957
			National Institutes of Health*	1957
			American Institute of Biological Sciences	1957
			The Geochemical Society	1958
			American Institute of Physics	1959
			Instrument Society of America	1959
			Consultants Bureau	1952
Derevoobrabat. prom-st.	Derevoobrabatyvayushchaya promyshlennost'	Telecommunications	Consultants Bureau	1956
	Elektrosvyaz	Entomological Review	Timber Development Association	1957
	Entomologicheskoe obozrenie	Pharmacology and Toxicology	Massachusetts Institute of Technology*	1959
	Farmakologiya i toksikologiya	Physics of Metals and Metallography	American Institute of Biological Sciences	1959
	Fizika metallov i metallovedenie		Consultants Bureau	1957
	Fiziologicheskii zhurnal im. I. M. Sechenova		Acta Metallurgica*	1957
	Fiziologiya rastenii	Sechenov Physiological Journal USSR		1957
	Geokhimiya	Plant Physiology		1957
	Fizika tverdogo tela	Geochemistry		1957
	Izmeritel'naya tekhnika	Soviet Physics-Solid State		1958
	Izvestiya Akademii Nauk SSSR: Otdelenie khimicheskikh nauk	Measurement Techniques		1959
		Bulletin of the Academy of Sciences of the USSR: Division of Chemical Sciences		1959

continued

Izv. AN SSSR, Otd. (tekh.). N(auk); Met(ali), i top.	(see Met. i top.)	Bulletin of the Academy of Sciences of the USSR; Physical Series	1	1954
Izv. AN SSSR Ser. fiz(ich).	Izvestiya Akademii Nauk SSSR: Seriya fizicheskaya	Bulletin of the Academy of Sciences of the USSR; Geophysics Series	1	1954
Izv. AN SSSR Ser. geofiz.	Izvestiya Akademii Nauk SSSR: Seriya geofizicheskaya	Izvestiya of the Academy of Sciences of the USSR; Rubber Technology	1	1958
Izv. AN SSSR Ser. geol.	Izvestiya Akademii Nauk SSSR: Seriya geologicheskaya	American Geological Institute	18	1959
Kauch. i rez.	Kauchuk i rezina	Research Association of British Rubber Manufacturers	1	1960
	Kinetika i kataliz	Consultants Bureau	3	1958
	Koks i khimiya	Coal Tar Research Association (Leeds, England)	1	1952
	Kolloidnyi zhurnal	Consultants Bureau	2	1957
Kristallografiya	Kristallografiya	American Institute of Physics	6	1958
Metall. i term. obrabot. metal.	Metallovedenie i termicheskaya obrabotka metallov	Acta Metallurgica	1	1957
Met. i top.	Metallurg	Acta Metallurgica	1	1960
Mikrobiol.	Metallurgiya i topliva	Eagle Technical Publications	1	1957
OS	Mikrobiologiya	American Institute of Biological Sciences	26	1959
	Optika i spektroskopiya	American Institute of Physics	6	1959
	Pochvovedenie	American Institute of Biological Sciences	1	1958
	Priborostroenie	British Scientific Instrument Research Association	1	1959
Pribory i tekhn. eksperimenta)	Pribory i tekhnika eksperimenta	Instrument Society of America	1	1957
Prikl. matem. i mekh.	Prikladnaya matematika i mekhanika	American Society of Mechanical Engineers	1	1958
PTÉ	(see Pribory i tekhn. eks.)			
Radiotekh.	Problemy Severa	National Research Council of Canada	12	1957
Radiotekh. i elektronika	Radiotekhnika	Massachusetts Institute of Technology*	1	1957
	Stanki i instrument	Massachusetts Institute of Technology*	2	1959
	Stal'	Production Engineering Research Assoc.	1	1959
Stek. i keram.	Steklo i keramika	Iron and Steel Institute	1	1956
Svaroch. proiz-vo	Svarochnoe proizvodstvo	Consultants Bureau	13	1956
Teor. veroyat. i prim.	Teoriya veroyatnostei i ee primeneniye	British Welding Research Association	4	1959
		Society for Industrial and Applied Mathematics	1	1956
Tsvet. Metall	Tsvetnyye metall	Primary Sources	1	1960
UFN	Uspekhi fizicheskikh Nauk	American Institute of Physics	66	1958
UKh	Uspekhi khimii	The Chemical Society (London)	1	1960
UMN	Uspekhi matematicheskikh nauk	London Mathematical Society	15	1960
Usp. fiz. nauk	(see UFN)			
Usp. khim(ii)	(see UFN)			
Usp. matem. nauk	(see UMN)			
Usp. sovr. biol.	Uspekhi sovremennoi biologii			
Vest. mashinostroeniya	Vestnik mashinostroeniya			
Vop. gem. i per. krov	Voprosy gematologii i pereivaniya krov	Oliver and Boyd	48	1959
Vop. onk.	Voprosy onkologii	Production Engineering Research Assoc.	4	1959
Vop. virusol.	Voprosy virusologii			
Zav(odsk.) lab(oratoriya)	Zavodskaya laboratoriya	National Institutes of Health*	1	1957
ZhAKh Zh. anal(it). khimii	Zhurnal analiticheskoi khimii	National Institutes of Health*	1	1957
ZhETF	Zhurnal eksperimental'noi i teoreticheskoi fiziki	Instrument Society of America	25	1952
Zh. eksperim. i teor. fiz.	Zhurnal fizicheskoi khimii	Consultants Bureau	7	1952
ZhFKh Zh. fiz. khimii	Zhurnal fizicheskoi khimii	American Institute of Physics	28	1955
ZhMEI Zh(urn), mikrobiol.	Zhurnal mikrobiologii, épidemiologii i immunobiologii	The Chemical Society (London)	7	1959
ZhNKh	Zhurnal neorganicheskoi khimii	National Institutes of Health*	1	1957
Zh(urn), neorgan(ich). khim(ii)	Zhurnal neorganicheskoi khimii	The Chemical Society (London)	1	1959
ZhOKh	Zhurnal obshchei khimii	Consultants Bureau	19	1949
ZhPKh	Zhurnal prikladnoi khimii	Consultants Bureau	23	1950
Zh(urn), prikl. khimii	Zhurnal prikladnoi khimii	Consultants Bureau	1	1960
ZhSKh	Zhurnal struktural'noi khimii	Consultants Bureau	1	1960
Zh(urn), strukt. khimii	Zhurnal struktural'noi khimii	American Institute of Physics	26	1956
ZhTF	Zhurnal tekhnicheskoi fiziki	National Institutes of Health*	1	1958
Zh(urn), tekhn. fiz.	Zhurnal vysshei nervnoi deyatel'nosti (im. I. P. Pavlova)			
Zh(urn), vyssh. nerv. deyat. (im. Pavlova)				

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